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A FURTHER INVESTIGATION OF THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.[1]

BY W. E. HENDERSON.

The chloride was prepared according to the directions given by Remsen and Gray,[2] with some modifications. The dehydrated acid potassium salt of paranitroorthosulphobenzoic acid and phosphorus pentachloride, in the ratio of 40 : 55 grams, are brought together in a mortar and intimately mixed. The mixture is put into an evaporating dish and placed on a sulphuric acid bath, previously heated to 150°. As soon as the action has been well started, the dish is removed and the reaction allowed to proceed without further heating. When it is complete, and the contents of the dish has cooled down to the ordinary temperature, the oily product is poured slowly into a salt-bottle containing ice-water, the bottle being frequently shaken during the process. The chloride is then shaken with repeated portions of water, until the water remains clear after shaking, and the chloride has become semi-solid. The water is then poured off, the brownish

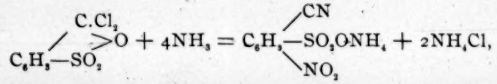
[1] From the author's dissertation, submitted to the Board of University Studies of the Johns Hopkins University, June, 1897, for the degree of Doctor of Philosophy. The work was undertaken at the suggestion of Professor Remsen, and carried on under his guidance.

[2] This JOURNAL, 19, 496.

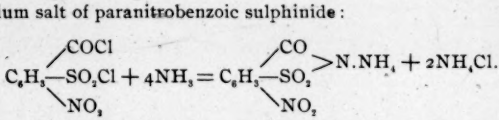
gummy chloride dissolved in chloroform, and the solution placed in a good-sized separating funnel. Ice-water is then added, and the contents of the funnel treated with successive portions of ammonia (desk ammonia diluted one-half). Shaking is continued after each addition until the odor of ammonia has disappeared, and ice is added from time to time as may be required.

When it is found that the odor of ammonia persists after a few minutes' shaking, the chloroform layer, which is often filled with a solid substance that has separated during the process, is drawn off, filtered, and dried with calcium chloride.

By this process all of the unsymmetrical chloride is converted into the ammonium salt of paranitroorthocyanbenzenesulphonic acid, according to the equation:



while the symmetrical chloride remains for the most part unchanged, though some of it is converted into the ammonium salt of paranitrobenzoic sulphinide:



It was found that working in this way the symmetrical chloride could be prepared in pure condition free from its isomer. The chloroform completely evaporates in a short time, leaving fine crystals of the symmetrical chloride. In case the evaporation is slow and incomplete, it may be concluded that not all of the unsymmetrical chloride has been removed. The yield was uniformly about 40 per cent of the theoretical.

From the water used to wash the chlorides a considerable amount of the original salt may be regained, as the reaction, under the conditions employed, is never complete.

An examination was made of the substance mentioned as separating in the chloroform solution of the chlorides during

the treatment with ammonia, and it was found to possess the following properties: It is insoluble in benzene, chloroform, acetone, ether, and ligroin; soluble in glacial acetic acid, from which it separates, on cooling, in colorless crystalline condition; insoluble in the cold in water, alcohol, and ammonia, but by long standing in these solvents it is dissolved with decomposition. It is soluble in them on boiling, with decomposition. It was dissolved in hot water, and the solution, which was acid in reaction, was neutralized with potassium carbonate. On adding an excess of hydrochloric acid to this solution and allowing it to cool, characteristic needles of the acid potassium salt of paranitroorthosulphobenzoic acid separated. These properties identify the substance as the anhydride of this acid. The formation of the corresponding anhydride of orthosulphobenzoic acid by the action of phosphorus pentachloride upon its acid potassium salt was observed by Sohon,[1] who made use of the reaction to prepare this anhydride in quantity.

As first obtained, the crystals of the symmetrical chloride resemble irregularly-shaped pieces of amber, both in color and in luster. On recrystallization from chloroform or ether they can be obtained perfectly colorless, and are often of very simple crystallographic form. The chloride crystallizes in the monoclinic system, and possesses a very remarkable crystallizing power, in which respect it differs noticeably from its isomer. Even in chloroform solution that is far from dry, crystals appear with the greatest ease.

The habit of the crystals differs very much according to the conditions of crystallization. Not infrequently, almost perfectly formed crystals of the simplest form—the oblique octahedron—were obtained, though for the most part the forms were much more complicated, pinacoid and dome faces, together with basal planes, being prominent. As a rule, the crystals were not suitable for crystallographic work, as the faces are rough, owing to the great solubility of the chloride. By proper precautions, however, fairly good ones were obtained for this purpose. The size of some of the crystals obtained was unusual for substances of this class. One crystal

[1] This JOURNAL, **20**, 257.

obtained with no special precautions, save letting a solution of the chloride stand undisturbed for several days, in a rather cool place, measured 3 × 2.5 × 1.5 cm., and weighed 11.2 grams.

The crystals are quite compact, their density being about 1.85. They melt at 98° (uncorr.). The chloride is quite stable when crystallized. Even in moist air the crystals were unchanged and retained their luster as long as they were in my possession.

An analysis for chlorine gave the following results:

0.2200 gram substance gave 0.2212 gram AgCl.

	Calculated for $C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases}$.	Found.
Cl	24.94	24.83

A crystallographic examination of the usual form of the crystals was made by Dr. F. P. King, in the mineralogical laboratory, and his measurements and description are here given:

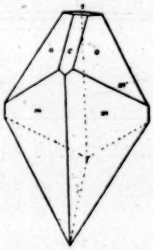
System monoclinic.

$s = +\frac{1}{2}P\overline{\infty} = (201)$
$o = +\ P\ \ = (111)$
$c = +\ P\overline{\infty} = (011)$
$m = \infty P\ \ = (110)$
$s : m' = 97° 35'$
$s : o = 120° 26'$
$s : c = 132° 45'$
$o : o = 96° 20'$
$o : c = 138° 10'$
$o : m' = 87° 31'$
$o : m = 138° 01'$
$m : m = 116° 50'$
$m : m' = 63° 10'$
$m : c = 122° 19'$

$\dot{a} : b : \dot{c} :: 0.898321 : 1 : 1.114179$

$\beta = 43° 11' 17''$

The figure is drawn on Dana's axes, showing β in front. Distortion, due to irregular growth, causes planes ċ and s generally to disappear at one extremity of ċ axis.



Since merohedrism is invariably present in respect to these planes the figure is drawn conformable to this distortion.

The measurements given are the actual measurements.

Action of Aluminium Chloride and Benzene upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

Hollis,[1] in his study of the action of these reagents upon the unsymmetrical chloride, tested their action upon one portion of the symmetrical chloride, and found the products to be identical in the two cases. A few experiments were made in confirmation of these results, and the same products, in general, were obtained. It was observed, however, that the reactions differ in the relative ease with which they are brought about. In the case of the symmetrical chloride, the reaction is a more vigorous one. On adding aluminium chloride to a solution of the symmetrical chloride in benzene, action begins at once at the temperature of the hand, and very little external heat, and that only in the latter stages of the operation, is required to complete the reaction. The application of much heat converts all of the product into thick tarry substances, from which nothing satisfactory could be obtained.

When the reaction was complete, the resulting product was isolated and purified in accordance with the directions given by Hollis. Repeated trials showed that, as in the case of the

[1] This JOURNAL, 23, 233.

unsymmetrical chloride, only one phenyl group could be introduced by this method. The resulting compound, paranitroorthobenzoylbenzenesulphone chloride, was identical with that derived from the unsymmetrical chloride. Owing, however, to the fact that so much more decomposition occurs in the reaction with the symmetrical chloride, the paranitroorthobenzoylbenzenesulphone chloride could not be obtained in perfectly pure condition. In appearance it agreed closely with that described by Hollis, forming very characteristic, greenish, rhombic crystals. These melted, not very sharply, at 174° instead of 177°, as observed by Hollis. Accordingly, to establish the identity of the two compounds, beyond any doubt, the material on hand was converted into the barium salt of paranitroorthobenzoylbenzenesulphonic acid. This was done by boiling the sulphone chloride with dilute hydrochloric acid until complete solution was effected; evaporating to dryness on a water-bath; dissolving the residue in hot water; and neutralizing with barium carbonate. On filtering the hot solution, and allowing it to cool, the barium salt separated.

The solution was slightly colored by impurities, and the long needles in which the salt crystallized were also somewhat colored. They were analyzed with the expectation that they would prove to be specimens of the salt described by Hollis as having 3 or 3.5 molecules of water of crystallization, inasmuch as they were formed under conditions favorable to the formation of salts of this particular type. Hollis found that this salt could be obtained with at least four different ratios of water of crystallization; *viz.*, 3, 3.5, 6, and 7 molecules, respectively.

The analysis gave the following results:

0.3087 gram substance lost 0.064 gram H_2O at 210°, and gave 0.0759 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 11H_2O$.	Found.
H_2O	20.90	20.73
Ba	18.29	18.23

The mother-liquor, in which the crystals remaining from analysis were redissolved, was warmed, but not boiled, with

bone-black to remove impurities. When filtered the solution was perfectly colorless, and on standing for some time, well formed, colorless, rhombic crystals appeared.

On analysis they gave the following results :

0.2804 gram substance lost 0.0405 gram at 210°, and gave 0.0736 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.44
Ba	18.29	18.03

On making a further supply of the salt, it was found that if the solution, after filtering from the excess of barium carbonate, was diluted to such an extent that no crystals separated on cooling, then, on slow evaporation under a bell-jar, the first crystals to appear were very long needles. As evaporation proceeded, these needles became much thicker, assuming prismatic proportions, and corresponded in appearance to the salt described by Hollis as having 6 molecules of water of crystallization. As growth proceeded, the crystals became dark in color, and the mother-liquor correspondingly clearer. Evidently the crystals absorbed the colored impurities in their growth. When the solution had become quite colorless, rhombic crystals of the salt containing 7 molecules of water of crystallization appeared. The larger prismatic crystals were carefully removed, and redissolved in water in order to see if the same phenomena would repeat themselves. This was in fact found to be the case, crystals of both types resulting. Without separating the crystals in this second experiment, water was added, and the crystals dissolved. The solution was then warmed briskly with bone-black, and filtered. From the filtrate, which was now colorless, nothing but the rhombic crystals having 7 molecules of water of crystallization could be obtained, although the conditions were widely varied.

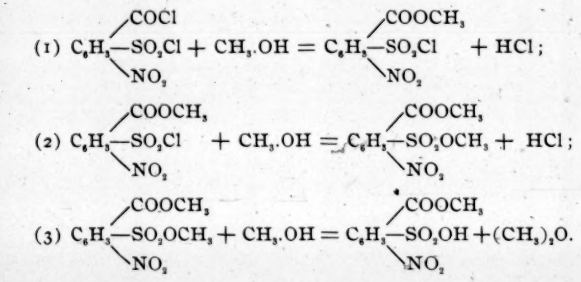
Analysis of these last crystals gave the following results :

0.2400 gram substance lost 0.035 gram at 210°, and gave 0.0637 gram $BaSO_4$.

	Calculated for $(C_{13}H_8O_6NS)_2Ba + 7H_2O$.	Found.
H_2O	14.40	14.58
Ba	18.29	18.27

Action of Alcohols upon the Symmetrical Chloride of Paranitro-orthosulphobenzoic Acid.

Kastle[1] found that when the chloride of paranitroorthosulphobenzoic acid (which he supposed to be an individual) was dissolved in alcohol and the solution boiled for some time, the acid ethereal salt of paranitroorthosulphobenzoic acid was the final product :



Kastle, it will be observed, gave the symmetrical formula to this mixture of chlorides. Several acid-ethereal salts were made, and a series of neutral salts of various metals described by him.

The action of the pure symmetrical chloride was studied in the same general manner, to see if the resulting products are the same as those resulting from the mixed chlorides.

1. *Action of Methyl Alcohol.*—A portion of the chloride was dissolved in methyl alcohol and the solution boiled until a drop added to water gave no precipitate of unchanged chloride. The alcohol was then distilled off, and the thick syrup remaining diluted with water. This was neutralized with barium carbonate and filtered. On cooling, the barium salt crystallized in shining mica-like plates, or in yellowish needles agreeing closely with the description given by Kastle.

Analysis :

0.2664 gram substance lost 0.0211 gram H_2O at 150°, and gave 0.0870 gram $BaSO_4$.

[1] This JOURNAL, II, 181.

	Calculated for $\left(C_6H_3\begin{cases}COOCH_3\\SO_2O\\NO_2\end{cases}\right)_2Ba + 3H_2O$.	Found.
H_2O	7.59	7.88
Ba	20.85	20.85

2. *Action of Ethyl Alcohol.*—In like manner the barium-ethyl salt was made. It also agreed perfectly with Kastle's description, crystallizing in fine, colorless needles forming tufts, from a not too concentrated solution. In case it is necessary to concentrate these solutions, it is of advantage to add a small quantity of alcohol to the solution, as this prevents any great amount of saponification, which otherwise takes place to a noticeable extent.

Analysis :

I. 0.2824 gram substance lost 0.0276 gram at 180°, and gave 0.0860 gram $BaSO_4$.

II. 0.2655 gram substance lost 0.0262 gram H_2O at 190°, and gave 0.0815 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}COOC_2H_5\\SO_2O\\NO_2\end{cases}\right)_2Ba + 4H_2O$.	Found. I.	Found. II.
H_2O	9.51	9.77	9.86
Ba	20.00	19.84	20.02

Kastle also found that by dissolving the mixed chlorides in cold alcohol, and allowing the solution to evaporate spontaneously, there separated crystals of the chloride of the acid ethereal salt of paranitroorthosulphobenzoic acid represented in equation (1). This same product was sought for, when pure symmetrical chloride was employed, but without success. Under all conditions crystals of unchanged chloride separated, or else it was found that it had been converted into the acid ethereal salt. In another trial, cold water was carefully added in small portions, since Kastle found that such treatment facilitated the separation of the substance ; the chloride alone appeared. Still other attempts were made to obtain the substance by adding a large amount of water to the solution of the chloride in alcohol, after it had stood for some time. In this way quite a precipitate was thrown down, and this

was filtered off and crystallized from ether. It always proved to be the symmetrical chloride, and none of the other substance was obtained.

Remsen and Karslake,[1] in working with the symmetrical chloride of orthosulphobenzoic acid, were unable to isolate the analogous compound, although from the mixed chlorides, by the action of alcohols, Remsen and Dohme[2] had obtained chloroethereal salts.

Inasmuch as the pure symmetrical chloride is relatively stable in cold alcohol, it can even be crystallized from warm alcohol with very little loss. It is possible that it is more stable than the chloroethereal salt, and that in consequence the latter, when formed, yields more readily to the further action of the alcohol than the chloride does. Hence, when the action begins it at once proceeds to the limit. The fact that the symmetrical chloride is rather sparingly soluble in cold alcohol, making the use of a concentrated solution impossible, may also be a factor in the case. Whatever may be the cause, the substance could not be obtained under any conditions that were devised.

Having in my possession a very small specimen of crystallized unsymmetrical chloride, it was submitted to the action of ethyl alcohol, under as nearly as possible the conditions employed by Kastle.

Crystals of a colorless substance were obtained, which in every respect agreed with Kastle's description of the chloride of the acid ethyl ethereal salt of paranitroorthosulphobenzoic acid. Crystallized from ether, they melted at 68°.

The conditions employed by Kastle in preparing the chloride would undoubtedly lead to a relatively large proportion of the unsymmetrical chloride, and it is to this chloride that the formation of the chloroethereal salt is apparently due.

The Action of Phenols upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

Remsen and Saunders,[3] in their investigation of the chlorides of orthosulphobenzoic acid, studied the action of phenol

[1] This JOURNAL, **18**, 819.
[2] *Ibid.*, **11**, 341.
[3] *Ibid.*, **17**, 347.

upon these substances, and from both the symmetrical chloride and the mixed chloride they obtained a normal diphenyl ether, and a red substance which was not further studied.[1] It was formed in small quantity, and was probably the corresponding sulphonphthalein. Later Remsen and McKee[2] obtained these same substances from both the symmetrical and unsymmetrical chlorides of the same acid. R. Meyer[3] obtained analogous substances by the action of various phenols upon phthalyl chloride. It seemed probable, therefore, that the chlorides of paranitroorthosulphobenzoic acid would yield similar derivatives, and a study was made of the reaction of the symmetrical chloride with a series of phenols. The products in some instances were exceedingly difficult to deal with, possessing properties that made it impossible to prepare them for analysis, but even in such cases there could be little doubt as to the general nature of the reactions that took place.

1. *Action of Phenol.*—A portion of the symmetrical chloride was brought together with somewhat more than double the molecular weight of phenol. The mixture was placed in a good-sized test-tube, and the temperature gradually raised by means of a sulphuric-acid bath. As soon as the phenol melts some slight action occurs, as is indicated by the bright-red color which the liquid assumes. At 115° hydrochloric acid is freely evolved, and the action is complete at 125°. The temperatures were ascertained by the use of a thermometer as a stirring rod. During the heating the color becomes a much more intense red, growing darker in shade, while the mixture becomes somewhat viscous, but does not solidify while hot.

When cool, the solid product was repeatedly extracted with boiling water, the aqueous solution being deep-purple. The colored material was very slowly removed from the insoluble residue in this manner, and so the process was continued with dilute alkali. The solid residue was dissolved in alcohol, purified with bone-black, and filtered. On cooling, needles of a straw-yellow color separated, which melted at 119° (uncorr.).

These proved to be the normal diphenyl ester of paranitro-

[1] This JOURNAL, **18**, 798.

[2] Ber. d. chem. Ges., **26**, 204.

orthosulphobenzoic acid, the formation of this substance being expressed by the equation:

$$C_6H_3(COCl)(SO_2Cl)(NO_2) + 2C_6H_5OH = C_6H_3(COOC_6H_5)(SO_2OC_6H_5)(NO_2) + 2HCl.$$

Analyses gave the following results:

I. 0.1627 gram substance gave 0.3398 gram CO_2 and 0.0510 gram H_2O.

II. 0.1999 gram substance gave 0.4180 gram CO_2 and 0.0600 gram H_2O.

III. 0.2649 gram substance gave 0.1561 gram $BaSO_4$.

	Calculated for $C_6H_3(COOC_6H_5)(SO_2OC_6H_5)(NO_2)$.	Found. I.	II.	III.
C	57.14	56.97	57.03	....
H	3.26	3.47	3.33	....
S	8.02	....	....	8.09

The substance possesses properties similar to those of the diphenyl ester of orthosulphobenzoic acid described by Remsen and Saunders. It is insoluble in water, and is not affected by hydrochloric acid or aqueous alkali. On heating for a short time with alcoholic potash the needles were transformed into a voluminous precipitate. This was filtered off, dissolved in water, and hydrochloric acid was added. On cooling, characteristic crystals of the acid potassium salt of paranitroorthosulphobenzoic acid separated. Analysis:

0.1392 gram substance lost 0.009 gram at 150° and gave 0.0385 gram K_2SO_4.

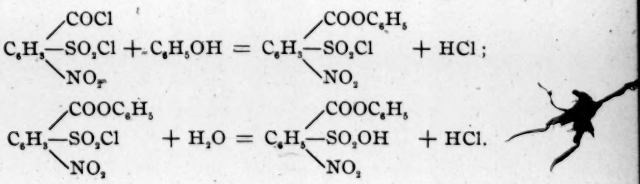
	Calculated for $C_6H_3(COOH)(SO_2OK)(NO_2) + H_2O$.	Found.
H_2O	5.95	6.51
K	13.65	13.35

No attempt was made to isolate the intermediate chloro-ethereal salt of the composition, $C_6H_3(COOC_6H_5)(SO_2Cl)(NO_2)$, or its amide

as was done by Remsen and McKee[1] in the case of the analogous ester of orthosulphobenzoic acid.

On evaporating the aqueous extract from the original insoluble residue almost to dryness on the water-bath, there was a deposit on the sides of the dish of scales possessing a beautiful bronze-green metallic luster. They formed a deep purple solution in alkalies, or magenta if the solution was very dilute, and orange-yellow in acids. On acidifying the alkaline extract with hydrochloric acid, this same substance was precipitated as a brownish, flocculent precipitate. It was, however, found to be impossible to obtain it in pure condition. The amount formed in the reaction is small, and its properties were such as to render work with it very difficult. The method of preparation is not satisfactory because, owing to the fact that the substance is soluble in acid solutions to an unusual extent for substances of this class, the solution had to be concentrated to such a degree as to render the precipitated substance very impure from acids and alkali salts. These could not be washed out without again dissolving the substance. From its properties, however, and its color reactions, there can be little doubt that the substance is a sulphonphthaleïn. It is always formed in considerable quantities in the reaction of phenol upon the symmetrical chloride.

It was noticed that the aqueous extract of the mass left after fusion was almost always decidedly acid in reaction, and it was thought that this might be due to the formation of an acid ethereal salt, whose formation could be thus expressed:



Accordingly, the solution was saturated with barium carbonate. Crystals, in the form of pearly scales, separated,

[1] This JOURNAL, 18, 799.

which upon analysis proved to be the neutral barium salt of paranitroorthosulphobenzoic acid.

0.2291 gram anhydrous salt gave 0.1386 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}COO\\SO_2O\\NO_2\end{cases}>Ba$.	Found.
Ba	35.85	35.57

This seems to indicate that the reaction is an incomplete one, even in the presence of an excess of phenol. No indication of an acid ester was observed.

2. *Action of Orthocresol.*—With orthocresol the reaction proceeds with more difficulty. A higher temperature was required (135° to 145°), and quite an amount of tarry material was obtained from which very little could be extracted. The product was warmed repeatedly with dilute alkali, the solution so obtained neutralized with hydrochloric acid, and distilled with steam for several hours to free it from cresol. The resulting solution was then evaporated to a small volume, and acidified with hydrochloric acid. A considerable precipitate was thrown down, which was easily filtered off and dried. In this condition it was a dark purple-red powder, lumps of which possessed a yellowish-bronze metallic luster. In dilute alkaline solution it forms a deep bluish-purple solution, while in acids it is crimson, or light-yellow if the solution is very dilute. It is an excellent indicator, especially with ammonia.

In the insoluble tarry substance the ester was sought for and obtained in small quantity only. As all of the tarry substance is soluble in alcohol and separates again from it on cooling, in much the same condition, the ethereal salt could not be isolated by crystallization from this solvent. By boiling the substance with benzene, purifying the filtrate with bone-black, and allowing the benzene to evaporate, an almost colorless, gummy substance was obtained, which, when dissolved in alcohol, crystallizes in small, colorless needles, which melt at 89° to 90°. They were not obtained in quantity sufficient for analysis, but there was no doubt that they were crystals of the diorthocresyl ester.

Apparently much more decomposition occurred in this re-

action than when paracresol was employed, probably in consequence of the higher temperature required for the reaction.

3. *Action of Paracresol.*—This reaction was conducted in the same manner as with phenol. No hydrochloric acid was evolved until a temperature of about 110° was reached, although after melting, the solution had steadily darkened to a deep, reddish-brown color. At 130°, after heating for several hours, hydrochloric acid ceased to be evolved. The product was treated as in the last experiment. The alkaline extract did not exhibit any marked color reactions, such as were observed in most of these experiments, being dull reddish-brown in both acid and alkaline solution.

The insoluble residue crystallized from alcohol in light-brownish, transparent crystals, which did not lose their color by repeated crystallization and boiling with bone-black. They melted at 117°. From benzene they crystallized in colorless needles or flat, narrow plates. These became opaque on exposure to the air, apparently through loss of benzene of crystallization.

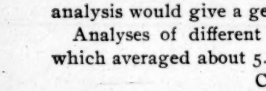
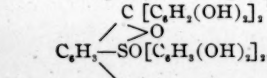
I. 0.2372 gram of the substance gave 0.5137 gram CO_2 and 0.0965 gram H_2O.

II. 0.2223 gram substance gave 0.1203 gram $BaSO_4$.

	Calculated for $C_6H_3\begin{cases}COOC_6H_4.CH_3\\SO_2OC_6H_4.CH_3\\NO_2\end{cases}$	Found. I.	II.
C	59.08	59.06	....
H	3.98	4.52	....
S	7.49	....	7.43

4. *Action of Hydroquinone.*—Action with hydroquinone occurs at 120° to 135°, the mixture at the same time becoming dark colored and viscous. On cooling, the product was powdered and treated with dilute alkali. It readily dissolved, without residue, forming a dark-red solution. In concentrated solution the addition of acid produces a voluminous precipitate, dark-brown in color, which, when washed and dried on paper, forms an almost black powder. A dilute solution of this powder is dark-red when alkaline, orange-yellow when acid.

From the way in which this powder was obtained, and owing to the fact that its solubility prevented repeated washing, it was evident that it would not give close analytical results for a definite formula. It was thought, however, that analysis would give a general idea of the composition.

Analyses of different specimens gave results for sulphur, which averaged about 5.5 per cent. The percentage required for the formula  , which represents the simplest fluoresceïn, is 7.43. The compound could hardly have been so far from pure as to occasion such a discrepancy in results as this. It would appear, therefore, that more than two molecules of hydroquinone enter into reaction with one molecule of the chloride. Should four molecules be involved in the reaction, leading to a compound of some such formula as  , the theoretical percentage of sulphur would be 6.00, which corresponds much more closely with the results obtained.

This is in accord with the observations of a number of workers in this laboratory—Lyman, Gilpin, Linn, and others who have worked on various sulphonfluoresceïns, and have found that in many cases four, six, and even eight phenol residues condense with one molecule of the anhydrous acid. Lyman[1] especially describes a tetrahydroquinone sulphonfluoresceïn derived from orthosulphoparatoluic acid. No ester was obtained.

5. *Action of Resorcin.*—The reaction of the chloride with resorcin is a much cleaner one and proceeds more readily than in the cases just described, leading, apparently, to an individual, well-characterized compound. During the reaction, which is complete at 125°, the mixture becomes almost perfectly solid, and when cool is quite brittle. It was reduced

[1] This JOURNAL, 16, 525.

to a reddish powder, and dissolved in sodium hydroxide, there being no insoluble residue. By the addition of an acid the sulphonfluorescein was thrown down as a chocolate-brown precipitate.

This was washed repeatedly by decantation and upon the filter, and was finally collected and dried on drying-paper. In this condition it is a light chocolate-brown powder. In dilute alkaline solution it possesses a slight fluorescence, being pink by transmitted and yellow by reflected light, suggesting eosin in a general way. It is interesting to note that the sulphonfluorescein of orthosulphobenzoic acid possesses a fluorescence which is almost indistinguishable from ordinary fluorescein, and that the introduction of a nitro group into the acid residue affects the color very much as the introduction of four bromine atoms into fluorescein. In acid solution the color is reddish-orange. Analyses of the compound gave the following results:

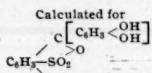
I. 0.1745 gram substance gave 0.3339 gram CO_2 and 0.059 gram H_2O.

II. 0.1467 gram substance gave 0.2820 gram CO_2 and 0.0432 gram H_2O.

III. 0.1732 gram substance gave 0.3345 gram CO_2 and 0.0571 gram H_2O.

IV. 0.2000 gram substance gave 0.1104 gram $BaSO_4$.

V. 0.1505 gram substance gave 0.0820 gram $BaSO_4$.



	Calculated for	Found.				
		I.	II.	III.	IV.	V.
C	52.66	52.18	52.42	52.67	....	....
H	3.46	3.76	3.27	3.66	....	....
S	7.39	....	....	....	7.57	7.48

An effort to obtain the anhydride was not successful. Some loss of weight was observed, but before the loss corresponded to one molecule of water the substance underwent deeper decomposition.

6. *Action of Pyrogallol.*—The product of this action dissolves readily in alkali, producing a very deep purple-black

color in concentrated solution, passing to grayish-violet as the solution is diluted. On the addition of acid it is precipitated as a black gelatinous mass. On attempting to collect the precipitate, it forms a sticky, black mass, which cannot be filtered successfully. It is best to evaporate to dryness, before filtration, and powder the residue. The powder can then be washed fairly clean. No ethereal salt was formed.

An estimation of sulphur showed that in this gallein, as in the case of the phthalein derived from hydroquinone, more than two pyrogallol residues had entered the acid residue. The indications were that six molecules had entered into one of the chloride. This also agrees with the observations of Lyman,[1] who describes a hexapyrogallol gallein of orthosulphoparatoluic acid. Probably a mixture of varying composition was obtained, and little importance was attached to the results save that they showed that no ester was formed in the reaction.

7. *Action of β-Naphthol*—It was hoped that here, as in the case of other monohydroxyphenols, an ester would be obtained. It was found, however, that very little action occurred, except such as was indicated by the development of a bright carmine color, until a temperature of 160° was reached. At this point hydrochloric acid was evolved, but the chloride itself undergoes decomposition. Nothing definite could be isolated from the reaction-products except unchanged β-naphthol.

Action of Aniline on the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

This action was studied to some extent by Remsen and Gray, but some points required further investigation. Some time was spent in an endeavor to obtain a method by which a good yield of the fusible or symmetrical anilide could be obtained. The yield in all cases tried is poor. The presence of the nitro group appears to complicate the reaction, leading to a secondary reaction, the course of which could not be followed. Upon bringing aniline and the chloride together a very vivid color was always observed, and the same was true

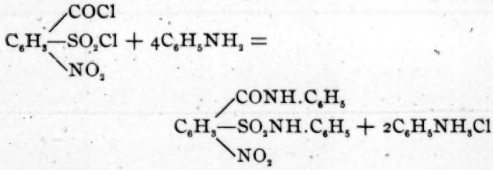
[1] This JOURNAL, 16, 527.

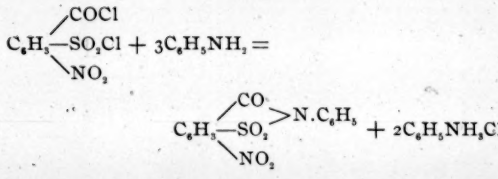
when it was necessary to employ alkali. The fact that such colors develop when nitro compounds are treated with alkali has been noticed in many instances, and some progress has been made in the study of these compounds. Jackson and Ittner[1] have recently reviewed this subject. If a solution of the symmetrical chloride in ether is slowly added to a similar solution of aniline, no appreciable amount of heat is generated. If the resulting solution is allowed to stand at the temperature of the room, action proceeds very slowly. The extent to which the action has progressed may be followed by observing the amount of aniline hydrochloride precipitated, as the other products of the reaction are soluble in ether. In this way it was found that 5 grams of chloride required about fifty hours for its conversion into anilide and anil. Results of an entirely similar character were obtained with chloroform as the solvent. By boiling the solution for an hour or so the reaction is complete.

The method employed was to bring the chloride and an excess of aniline—somewhat more than four molecules—together in chloroform solution. The solution was then boiled for about an hour, after which the chloroform was distilled off. During the boiling, as well as the distillation, more or less bumping occurs in consequence of the separation of aniline hydrochloride, and constant shaking of the flask is sometimes necessary. The residue, which is in a thick, gummy condition, in consequence of the presence of an excess of aniline, was digested with water acidulated with hydrochloric acid. The excess of aniline is thus removed and the reaction-product obtained as a reddish-brown solid substance. This was treated with dilute sodium hydroxide, in the cold, all lumps of the solid substance being broken up with a stirring rod. The undissolved substance is largely the anil. This was filtered off. The anilide which is in solution is obtained by acidifying the alkaline solution. It separates immediately as a curdy, colorless precipitate, though it is frequently discolored by impurities. In such case it was generally easily purified by redissolving in alkali and pouring the solution into a slight excess of acid.

[1] This JOURNAL, 19, 199.

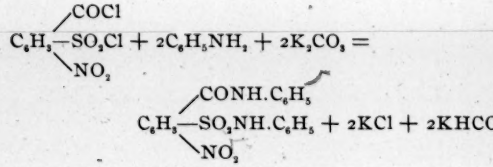
In all cases a considerable amount of anil was observed. This was true even when the ratio of chloride to aniline was as great as one molecule to eight or ten. The reactions involved are:





On the whole, the reaction seemed to take place most satisfactorily in chloroform solution.

A number of experiments were made to see if the yield could be increased by employing a modification of the Schotten-Baumann reaction[1] for the preparation of anilides. For this purpose an ethereal solution of the chloride was added to a like solution of aniline, in which was suspended anhydrous potassium carbonate. The proportions of the substances were those demanded by the equation:



Very little anilide was, however, obtained, but in its place a substance soluble in water, of acid reaction, capable of form-

[1] Ber. d. chem. Ges., **17**, 2545; **23**, 3430.

ing salts and yielding several well characterized derivatives.

The acid substance appeared to be an anilido acid. The barium salt was extremely soluble, crystallizing when the solution had gone nearly to dryness in thick radiating needles. Only a small amount was obtained, and it was undoubtedly impure. The analysis gave the following results:

0.2225 gram salt lost 0.0405 gram H_2O and gave 0.0530 gram $BaSO_4$.

	Calculated for $\left[C_6H_3(CO.NH.C_6H_5)(SO_2O)(NO_2)\right]_2Ba + 9\frac{1}{2}H_2O$.	Found.
Ba	14.42	14.00
H_2O	18.00	18.20

There was, of course, no evidence as to which acid group combines with the aniline residue. The formation of this substance could be explained by the following reactions:

1. $C_6H_3(COCl)(SO_2Cl)(NO_2) + C_6H_5NH_2 = C_6H_3(CO.NH.C_6H_5)(SO_2Cl)(NO_2) + HCl.$
2. $K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O.$
3. $C_6H_3(CO.NH.C_6H_5)(SO_2Cl)(NO_2) + H_2O = C_6H_3(CO.NH.C_6H_5)(SO_2OH)(NO_2) + HCl.$

The anilide is rather sparingly soluble in alcohol, from which it is deposited, on cooling, in microscopic needles. These melt at 222°, as stated by Remsen and Gray. It is also soluble in chloroform, ether, and glacial acetic acid, but does not form well defined crystals from any solvent. It is soluble in alkali, and is reprecipitated by acids unchanged.

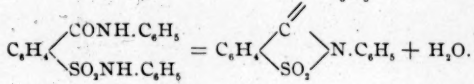
The anil is also soluble in alcohol, glacial acetic acid, etc. It crystallizes in much better formed needles than does the anilide. These melt at 183°. On boiling the anil for some time with aniline it is converted into the anilide:

$$C_6H_3(CO)(SO_2)(NO_2)>N.C_6H_5 + C_6H_5NH_2 = C_6H_3(CONH.C_6H_5)(SO_2NH.C_6H_5)(NO_2).$$

In none of these reactions was any infusible aniline observed.

Action of Phosphorus Oxychloride on the Fusible Anilide.

Remsen and Hunter[1] found that when either of the anilides of orthosulphobenzoic acid is treated with phosphorus oxychloride, or similar dehydrating agents, a molecule of water is abstracted with the formation of a new substance. A careful study of the compound led to the belief that it is a dianil, and that its formation and structure are expressed in the following equation:



A corresponding study of the fusible anilide of paranitroorthosulphobenzoic acid was undertaken. The method employed in this study was as follows: A tubulated retort of convenient size was fused to the inner tube of a small condenser. This was done to avoid rubber connections which are attacked by phosphorus oxychloride. Another satisfactory plan is to have the neck of the retort of the same size as the inner tube of the condenser. The ends are placed in contact and the tubes bound in position by wrappings of asbestos paper. Over the joint so made a tight rubber tube is drawn.

A convenient amount (50 cc.) of phosphorus oxychloride was placed in the retort, and the anilide (5 grams) added through the tubulus. On boiling with an inverted condenser, the anilide soon dissolved with evolution of hydrochloric acid, and the solution became yellow or orange in color. The boiling was continued as long as hydrochloric acid was evolved. The oxychloride was then distilled off under diminished pressure, care being taken to shake the retort constantly during the distillation, as toward the end of the operation there is a tendency to bump violently, if this precaution is omitted. The product remaining, spattered over the walls of the retort, is a greenish-yellow solid. Water was then added, and the whole allowed to stand for a few hours to dissolve the phosphoric

[1] This JOURNAL, **18**, 810.

acid formed in the reaction. In case the anilide is not perfectly dry, a more energetic reaction occurs, and on distilling off the oxychloride, the product remains as a dark, gummy substance. This should be spread over the sides of the retort while still warm. On cooling, water is added, and gradually the gum disappears, and in its place is found the same yellow product just described. After drying this substance, it can be crystallized from acetone, benzene, or glacial acetic acid, after purification with bone-black. From these solvents it crystallizes in small yellow needles resembling quinone. From acetone the needles are more orange in color than those from glacial acetic acid, apparently because of their greater compactness. In case glacial acetic acid is used, care should be taken to avoid unnecessary heating, as continued boiling with this reagent causes a decomposition which will be spoken of presently. These needles melt at 208°. Analyses gave the following results:

I. 0.3822 gram substance gave 0.8334 gram CO_2 and 0.1272 gram H_2O.

II. 0.2645 gram substance gave 0.5812 gram CO_2 and 0.0910 gram H_2O.

III. 0.2023 gram substance gave 0.1283 gram $BaSO_4$ (Liebig).

IV. 0.2061 gram substance gave 0.1280 gram $BaSO_4$ (Liebig).

V. 0.1853 gram substance gave 16.73 cc. N (standard).

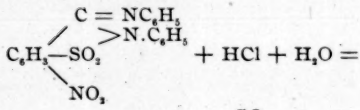
	Calculated for $C_6H_5-SO_2-\overset{\overset{N.C_6H_5}{\|}}{C}(NO_2)-N.C_6H_5$.	Found.				
		I.	II.	III.	IV.	V.
C	60.11	59.47	59.93	....	....	....
H	3.44	3.69	3.82	....	....	....
S	8.45	....	....	8.70	8.52	....
N	11.08	....	....	....	....	11.35

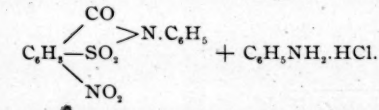
For analyses I and II, I am indebted to Mr. Nakaseko, of this laboratory, who kindly made them for me.

Action of Reagents upon the Dianil of Paranitroorthosulphobenzoic Acid.

1. *Action of Hydrochloric Acid.*—When the dianil is boiled

for some time with concentrated hydrochloric acid the yellow color of the substance disappears and the dianil is converted into a colorless substance, without, however, passing into solution. After crystallization from alcohol the substance so formed was obtained in the form of small, colorless needles. These melted at 183° and possessed all the properties of the anil, which, in fact, they proved to be. The reaction may be thus expressed:





This reaction also explains the fact that some anil was always obtained in making the dianil from the anilide. Hydrochloric acid is formed in the reaction, and in turn reacts with some of the dianil in the sense of the equation just given.

2. *Action of Alcoholic Potash.*—On boiling the dianil with alcoholic potash for a time, the solution turned red, and nothing but tarry products were obtained. In this respect the dianil differs from the dianil of orthosulphobenzoic acid which, under similar conditions, is transformed into infusible anilide. This observation is, however, in accord with the fact that the nitro derivative is in general much less stable in the presence of alkali.

3. *Action of Glacial Acetic Acid.*—When the dianil is boiled with glacial acetic acid for some time, the color of the solution changes to a much lighter shade of yellow, or disappears. On evaporating the solution to a small volume, and allowing the solution to cool, a colorless substance separates. This is the infusible anilide. It could not be obtained in crystals from any solvent, but always separated in flakes. It does not melt or undergo change at 340°. Like the fusible anilide it is soluble in alkali, but on acidifying the solution it does not at

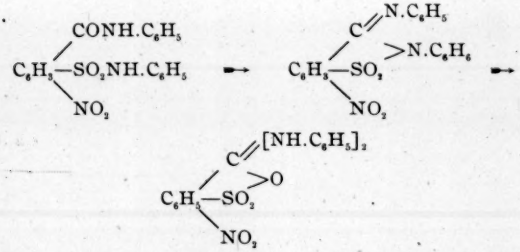
once reappear. On standing for some time, however, it gradually separates in pure form. In this particular my observation differs from that of Remsen and Gray,[1] who state that this anilide is decomposed by alkali.

A sample that had been repeatedly precipitated gave the following results on analysis:

I. 0.1607 gram substance gave 13.88 cc. N (standard).
II. 0.2195 gram substance gave 0.1285 gram $BaSO_4$.
III. 0.1357 gram substance gave 0.0807 gram $BaSO_4$.

	Calculated for	Found. I.	II.	III.
N	10.58	10.85	....	....
S	8.06	....	8.00	8.16

By this series of transformations, therefore, it is possible to pass from one anilide to the other, the successive steps being:



This is of especial interest as affording a method of passing from a derivative of the symmetrical chloride to a substance derived from the unsymmetrical chloride by steps that can be clearly followed.

Conclusions.

In the course of this investigation several facts have been established:

1. By the methods described the symmetrical chloride of paranitroorthosulphobenzoic acid can be obtained in fine crys-

[1] This JOURNAL, 19, 496.

talline condition perfectly free from its unsymmetrical isomer, with an average yield of 40 per cent.

2. By treatment of the chloride with benzene and aluminium chloride, only one chlorine atom can be replaced by the phenyl group.

3. With alcohols the symmetrical chloride yields directly the acid ester of paranitroorthosulphobenzoic acid, no evidence of an intermediate chloroethereal salt having been observed.

4. With phenols two series of derivatives are obtained.

(*a*) With monohydroxyphenols both esters and sulphophthaleïns are formed, the former predominating.

(*b*) With polyhydroxyphenols no esters were obtained, but compounds of the unsymmetrical type, usually containing more than two phenol residues.

5. With aniline, an anil and an anilide of symmetrical constitution are formed.

6. With phosphorus oxychloride the anilide, by loss of water, forms a dianil.

7. This dianil undergoes transformation with

(*a*) Glacial acetic acid forming an anilide of unsymmetrical constitution.

(*b*) Hydrochloric acid forming the anil.

(*c*) Alcoholic potash, with the formation of colored decomposition-products.

THE COMPOSITION OF A WOOD OIL.[1]

By G. S. Fraps.

INTRODUCTION.

The destructive distillation of wood gives rise to a great number of compounds. The products, crude wood spirit, wood vinegar, wood creosote, wood tar, and the gases, have been the subject of frequent chemical investigation, with the result that a large number of compounds have been detected in them. Wood vinegar contains the whole series of satura-

[1] From the author's dissertation submitted to the Boafd of University Studies of the Johns Hopkins University, June, 1899, for the degree of Doctor of Philosophy. The work was undertaken at the suggestion of Professor Remsen, and was carried on under his guidance.

ted fatty acids[1,2] up to, and including caproic acid: formic acid, acetic acid, propionic acid, butyric acid, valeric acid, and caproic acid.[1] It also contains valerolactone,[3], pyrocatechol,[4] and three unsaturated acids,[2] α-crotonic acid, β-crotonic acid, and angelic acid. Wood creosote[5] is a mixture of phenols, and their acid ethers—phenol, the three cresols, the xylenols (1, 3, 4 and 1, 3, 5), orthoethylphenol, guaiacol, methylguaiacol, ethylguaiacol, propylguaiacol, and finally the dimethyl ethers of pyrogallic acid, methylpyrogallic acid, and propylpyrogallic acid. The tendency to form homologous series comes out very plainly in the list just given.

Besides methyl alcohol and methyl acetate, the lower boiling portions of crude wood spirit contain methyl formate,[6] methyl acetate,[7] acetone, methylethylketone,[8] allyl alcohol,[9] dimethylacetal,[10] acetic aldehyde,[8] methylamine, and ethyl alcohol.[11] The presence of the last named requires confirmation, since, in spite of the fact that many chemists have worked on crude wood spirit, it has been reported but once. A still greater number of compounds have been detected in the less volatile portions of crude wood spirit; the list is a long one, and the compounds again range themselves in homologous series. We find isobutyl alcohol,[12] isoamyl alcohol,[13] and indications that higher alcohols[12] are present; methylpropylketone,[14] ketopentamethylene, or cyclopentanone or adipic ketone,[15] ketohexamethylene, or pimelic ketone,[12] and an unsaturated ring ketone, α-methyl-β-ketopentamethenylene[13] or methylcyclopentanone, C_6H_8O; toluene,[16,17] xylene,[16,17]

[1] Barre: Compt. rend., **68**, 1222.
[2] Krämer and Grodzki: Ber. d. chem. Ges., **11**, 1356.
[3] *Ibid.*, **17**, 1369.
[4] Jahresbericht, 1864, 651.
[5] Behal and Choay: Bull. Soc. Chim. (Paris), [3] **11**, 703; Compt. rend., **118**, 1341; **119**, 166.
[6] Mabery: This Journal, **5**, 256.
[7] Völckel: Ann. Chem. (Liebig), **86**, 66.
[8] Krämer and Grodzki: Ber. d. chem. Ges., **9**, 1920.
[9] *Ibid.*, **7**, 1492.
[10] Ann. Chem. (Liebig), **132**, 240.
[11] Ber. d. chem. Ges., **13**, 661.
[12] Looft: Ber. d. chem. Ges., **27**, 1542.
[13] Wislicenus and Looft: Ann. Chem. (Liebig), **275**, 366.
[14] Vladesco: Bull. Soc. Chim. (Paris), [3], **3**, 510.
[15] Wislicenus and Hentzschel: Ann. Chem. (Liebig), **275**, 318.
[16] Krämer and Grodzki: Ber. d. chem. Ges., **9**, 1920.
[17] Cahours: Ann. Chem. (Liebig), **76**, 286.

cumene,[1,2] and cymene;[2] pyridine[3] and methylpyridine.[4]

According to E. Looft,[3] the term "wood oil" is used to designate the low-boiling portions of wood tar, and likewise the less volatile portions and residues of crude wood spirits. It is self-evident that there must be common constituents of these two products, but there may also be considerable difference.

The compounds reported as present in wood tar are: propionic aldehyde,[5] furfural[6] and methylfurfural;[7] methylfurane,[8] dimethylfurane,[5] trimethylfurane;[5] toluene,[5] xylene,[5] and cumene;[9] pyroxanthine,[10] which is a condensation-product of furfural with adipic ketone;[11] and lastly, two ketones,[12] one $C_7H_{10}O$, methylcyclohexanone; the other is still under investigation.

The above is a list of the compounds whose presence has been from time to time reported in the various liquid products from the distillation of wood. The proportions in which they are present, if they are present, is dependent upon the conditions of the distillation, the kind of wood used, etc. It is interesting to note that the list includes no mesitylene, phoron, mesityl oxide, or other compound that could justly be called a condensation-product of acetone. The statement that "condensation-products of acetone" are formed in the distillation of wood is unwarranted, though it has been made over and over again.

PART I.

INVESTIGATION OF THE WOOD OIL BOILING BELOW 140°.

The material used in this investigation is obtained from hard-wood tar. The tar is distilled, the distillate treated with caustic potash, and again distilled. The last distillate

[1] Cahours: Ann. Chem. (Liebig), **76**, 286.
[2] Krämer and Grodzki: Ber. d. chem. Ges., **9**, 1920.
[3] Wislicenus and Looft: Ann. Chem. (Liebig), **275**, 366.
[4] Looft: Ber. d. chem. Ges., **27**, 1542.
[5] Fischer and Laycock: Ber. d. chem. Ges., **22**, 101.
[6] Hill: *Ibid.*, **10**, 936.
[7] Hill: *Ibid.*, **22**, 607.
[8] E. Harries: *Ibid.*, **31**, 37.
[9] Volckel: Ann. Chem. (Liebig), **86**, 331.
[10] Ann. Chem. (Liebig), **21**, 43.
[11] Ber. d. chem. Ges., **29**, 1838.
[12] Behal: Compt. rend., **125**, 1036; **126**, 46.

was that received for examination. As will be seen in Part II, the treatment with alkali did not remove all acid substances. The oil was of a brownish-red color, and semitransparent. Seventeen liters of the oil were distilled, a short Hempel tube filled with glass beads being used, and fractions at intervals of 15° being collected up to 150°. To prevent the vapors from penetrating the cork stoppers, which they did at first with the greatest readiness, the corks were covered with a strong solution of sodium silicate and dried. This was a very effective way of rendering the stoppers vapor-tight.

The first distillates were cloudy. The cloudiness was removed by calcium chloride. They were subjected to a careful fractional distillation, with the same Hempel tube, collecting the fractions at intervals of 5°, except the first three, which boiled at 54° to 57°, 57° to 61.5°, 61.5° to 65°. After six fractionations, 42 per cent of the oil had passed over below 140°. The oils accumulated decidedly in the fractions 57° to 61°.5, 100° to 105°, and 130° to 135°, with another accumulation, not so marked, at 75° to 80°. The table shows the relative sizes of these fractions, expressed in percentages of the total oil.

Fraction	54°–57°	57°–61.5°	61.5°–65°	70°–75°	75°–80°
Per cent	2.3	**2.6**	1.3	1.2	**1.7**
Fraction	80°–85°	95°–100°	100°–105°	105°–110°	
Per cent	1.4	2.9	**5.2**	4.5	
Fraction	125°–130°	130°–135°	135°–140°	54°–140°	
Per cent	1.4	**4.5**	1.7	42	

The first fractions were almost colorless; in general terms, the color became darker as the boiling-point became higher, passing from colorless through light-yellow, bright-yellow to dark-yellow. The change was not regular. The color was always lighter when the oil had been freshly distilled than after it had stood for some days.

The fractional distillation above described was carried out by Mr. E. W. Magruder, to whom the thanks of the author are due.

I. SOLUBILITY.

All of the fractions were soluble in water to some extent. To determine the solubility, about 10 cc. of each fraction were

shaken well in a burette with 40 cc. water, and the loss in volume measured. The high solubility of the low-boiling fractions was unexpected. The solubility decreased with increase in boiling-point of the fraction.

Fraction.	Per cent dissolved.	Fraction.	Per cent dissolved.
57°–61.5°	52	80°–85°	27
61.5°–65°	35	85°–90°	23
65°–70°	33	90°–95°	16
70°–75°	30	95°–100°	12
75°–80°	28	100°–105°	12

II. KETONES AND ALDEHYDES REMOVED BY ACID SODIUM SULPHITE.

Preliminary trials to effect combination between the oil and a solution of acid sodium sulphite were unsuccessful. It was soon found, however, that combination takes place with great readiness when a very concentrated solution of the salt is used. The solution of the acid sulphite was made by passing sulphur dioxide into a cooled solution of caustic soda (1 : 3) until the required weight was absorbed. This occurs approximately when the precipitate of sodium sulphite that first forms has redissolved. Each fraction was well shaken with a quantity of the solution so prepared, when many of them became so warm that it was thought necessary to cool with water. After standing for some time, the oil and aqueous solution were squeezed from the precipitate through a cloth, and, when the precipitate was sufficiently large, it was placed in a press and as much of the oil pressed from it as possible. The oil was treated with the solution of the sulphite a second, and in some cases a third, time.

The character of the precipitate varied with the boiling-point of the fraction from which it was separated. The more volatile oils gave crystalline precipitates easy to handle, but as the boiling temperature increased, the precipitates became more and more flocculent in character, shading into gelatinous, until those from the fractions over 120° were very like aluminium hydroxide.

From the weight of the precipitate from each fraction, dried on drying-paper in the press, the approximate weight of

ketone in the corresponding fraction was calculated, making the assumption that the volume of the ketone is one-half the weight of the precipitate. Aldehydes were present with the ketones, but in such quantity as not to affect this approximation. The figures are crudely approximate, but serve to give an idea of the relative percentages of ketones in the fractions. The table shows the occurrence of the maximum percentages of ketones.

Fraction	70°–75°	75°–80°	80°–85°	95°–100°	100°–105°	105°–110°
Per cent	12	14	10	17	18	11
Fraction	110°–115°	120°–125°	125°–130°	130°–135°	57°–140°	
Per cent	3	5	18	9	mean 10	

From the above figures one might expect ketones boiling between 75°–80°, 100°–105°, 125°–130°, with the probability of one boiling below 85°. The maximum percentages of ketones are in the largest fractions in the case of fractions 75°–80° and 100°–105°. There is no accumulation of ketone in the fraction 57°–61.5°, and the highest percentage occurs in the fraction 125°–130° instead of in 130°–135°, which is three times as large. The table shows also the value of a sixfold fractional distillation with a Hempel tube, applied to a complex mixture. The separation of the ketones can hardly be called satisfactory.

(1) *Methylethylketone* (78°).

The sulphite compounds from the fractions boiling below 110° were distilled separately with a solution of sodium carbonate. The distillates had an aldehyde-like odor, and gave instantly a heavy mirror with ammoniacal silver oxide (Tollens' solution). With the exception of certain fractions, with which an attempt was made to identify the aldehyde, as described below, the ketones were salted out with potassium carbonate and fractionated with the others. The remainder of the sulphite compounds were decomposed with a solution of sodium carbonate under a reflux condenser and separated in the usual way. After drying all the fractions with calcium chloride they were fractionated. The distillates accumulated in the fractions 80°–85°, 100°–103°, 128°–131°, which correspond to certain ketones. The ketone boiling at 80°–85° could

hardly be other than ethylmethylketone, which has been separated by Krämer and Grodzki[1] and by Vladesco[2] from crude wood spirit by means of the sulphite compound. Acetone was also present in small quantity.

(2) *Valeric Aldehyde* (*103°*).

Every ketone fraction gave the silver test for aldehydes. The aldehydes in the distillates from the sulphite compounds precipitated from the fractions 57.5°–61.5°, 85°–90°, were oxidized with ammoniacal silver oxide, and an attempt made to separate sufficient of the silver salt of the corresponding acid for analysis. This failed on account of the small quantity of aldehyde present.

Valeric aldehyde was detected in the ketone fraction 100°–103°. According to Herz,[3] ketones require many hours to be oxidized by a solution of 6 grams potassium bichromate and 8 grams sulphuric acid in 50 cc. water, even at an elevated temperature. Fraction 100°–103° became warm when shaken with this mixture. After standing a few minutes, the oil, which contained the fatty acid, was separated and distilled from potassium carbonate. The residue was distilled with dilute sulphuric acid, the distillate neutralized, silver nitrate added, and the precipitate redissolved by heating. A silver salt which had the composition of silver valerate, crystallized from the filtered solution.

0.4051 gram silver salt gave, on ignition, 0.2094 gram silver.

	Calculated for $C_5H_9O_2Ag$.	Found.
Ag	51.67	51.69

The fraction 128°–131° was treated with chromic acid in a similar manner, but while a small quantity of acid was formed it was not enough for the preparation and analysis of the silver salt. Valeric aldehyde has not before been detected in the products of the distillation of wood. While it was not possible to identify any other aldehydes in this wood oil, other aldehydes are probably present.

[1] Ber. d. chem. Ges., 9, 1920.
[2] Bull. Soc. Chim. (Paris), [3], 3, 510.
[3] Ann. Chem. (Liebig), 186, 257.

According to Krämer and Grodzki,[1] acetic aldehyde is usually found in the most volatile distillate from crude wood spirits. Fischer and Laycock[2] report the presence of propionic aldehyde in wood tar. This gives a good basis for the belief that the process of destructive distillation of wood gives rise to an homologous series of aldehydes, corresponding to the homologous series of acids found in wood vinegar. Since acetic aldehyde, propionic aldehyde, and valeric aldehyde are already detected, corresponding to acetic acid, propionic acid, and valeric acid, one could predict that formic aldehyde, butyric aldehyde, and caproic aldehyde will be detected and fill the gaps.

(3) *Methyl-n-propylketone* (*102°*).

The presence of methyl-*n*-propylketone in crude wood spirits was established by Vladesco. The ketone fraction 100°–103° contains this ketone. Treated with amyl nitrite and hydrochloric acid, the fraction gave an isonitroso compound which melted at 51.5° to 52.5° after recrystallization from petroleum ether. The melting-point of the isonitroso compound of methyl-*n*-propylketone is 48° to 51°.

(4) *Adipic Ketone—Methyl-n-butylketone.*

Claisen, in 1875, separated a ketone from crude wood spirits to which he gave the formula $C_6H_{10}O$. Wislicenus and Hentzschel[3] later examined this compound, and gave it the formula C_5H_8O. They found it to be identical with the ketone formed by distilling the calcium salt of adipic acid, which yields glutaric acid by oxidation, quantitatively, and otherwise shows that it is a ring ketone—adipic ketone, or ketopentamethylene.

The ketone under examination, in the ketone fraction 128°–131°, was at first assumed to consist of adipic ketone, and confirmation was sought in the formation of the oxime. To 10 grams in a little alcohol, 4 grams hydroxylamine and a few drops of a saturated solution of sodium carbonate were added, and the mixture heated on the water-bath. The oil which

[1] Ber. d. chem. Ges., **9**, 1920.
[2] *Ibid.*, **22**, 101.
[3] Ann. Chem. (Liebig), **275**, 318.

separated did not solidify over night, as it was expected to do; did not solidify at all, even after long exposure to a temperature below zero. It distilled completely at 185° to 188° and still refused to solidify. Adipic oxime behaves differently. It melts at 56.5°. Adipic ketone is oxidized almost quantitatively by nitric acid to glutaric acid. The ketone in question, oxidized with nitric acid of sp. gr. 1.20 by the method of Wislicenus, yielded only one-sixth as much solid acid as it ought to yield were it pure adipic ketone. The acid formed the zinc salt characteristic of glutaric acid, more soluble in cold than in warm water.

Only a portion of the fraction was adipic ketone. The other ketone present is probably methyl-*n*-butylketone (127°–128°). This is next in the series after methyl-*n*-propylketone, and its boiling-point corresponds to that of the ketone we should expect to find in the fraction of the oil 125°–130° on account of the accumulation of ketone in it. Although the fraction boiling at 130° to 135° was three times larger than that boiling at 125° to 130°, the latter contained twice as much ketone as the former. This would lead us to look for a ketone boiling between 125° and 130°. Since methyl-*n*-butylketone boils at 127° to 128°, and is the next member in the series dimethylketone, methylethylketone, methyl-*n*-propylketone, it is reasonable to suppose that the ketone in question is methyl-*n*-butylketone. Sufficient material to decide this point was not available.

(5) *Mesityl Oxide (130°) (Not Present).*

Mesityl oxide unites with acid sodium sulphite to form a compound very easily soluble in water, and easily decomposed by concentrated caustic soda to reform mesityl oxide. "Condensation-products of acetone, as mesityl oxide, phoron, etc.," have often been stated to exist in the products of the distillation of wood, but they have never been separated and described. A test for mesityl oxide in the wood oil under investigation gave negative results.

The sulphite solution which had been shaken with fraction 125°–130°, and from which all solid ketone sulphite compound had been removed, was distilled with a large excess of

caustic soda. A very few drops of oil came over, which did not possess the characteristic odor of mesityl oxide. Mesityl oxide was therefore absent. The liquid in the flask assumed a deep-brown color. It was neutralized with sulphuric acid, cooled, when most of it becomes solid from the crystallized sodium sulphate, and extracted with alcohol. On evaporation, the extract left a reddish-brown, tarry mass with the odor of the oil from burning paper.

III. ETHEREAL SALTS.

The treatment with acid sodium sulphite had diminished the size of the fractions considerably, a loss perhaps due in great part to their solubility. The residues were dried with potassium carbonate and once fractionated. The distillates were colorless to yellow when freshly distilled, becoming darker on standing. As methyl formate and methyl acetate have been found in crude wood spirits, the presence of ethereal salts was suspected in the wood oil under investigation. To a few drops of different fractions in test-tubes, phenolphthalein and one drop of a very dilute solution of caustic soda were added. The red color disappeared in a few seconds, indicating ethereal salts.

The ethereal salts were saponified with an aqueous solution of caustic soda (1 : 4). Heating the oil and alkaline solution under a reflux condenser was first tried, but the operation was very slow, and other reactions than saponification took place; the solution became dark-red, and the oil itself became highly colored. Saponification in the cold by shaking the oil and solution of caustic soda together for about fifteen hours was much more satisfactory. While the alkali changed in color, the change was not so great as when heat was used. The shaking arrangement consists simply of two boards bolted to a revolving shaft and about 3 inches from it. The bottles, holding 500 cc., were held firmly in place by rawhide thongs, which passed through holes in the boards, around the bottles, and were secured by wedges in the holes. An electric motor furnished power. This simple arrangement did effective work. The oil and alkaline solution were in an emulsified condition all the time it was in motion, and the ethereal salts were

rapidly and completely saponified. The bottle was placed on the shaker in the afternoon, and removed the next morning.

The oil was separated from the solution of caustic soda and measured. The loss was supposed to represent roughly the amount of ethereal salt saponified. Taking the volume of the oil that had been treated with sulphite as the basis, it varied from 80 per cent in the fraction 57.5°–61.5° to 22 per cent in the fraction 135°–140°. No attempt was made to calculate the percentage of ethereal salts in the original oil, on account of the loss due to treatment with sodium bisulphite. The percentage of ethereal salts decreases with rise in boiling-point. One might conclude from this that the quantity of organic acids in the corresponding wood vinegar decreases with increase in the boiling-point of the acid.

(1) *Alcohol—Nitriles.*

The solution of caustic soda contained the alcohol and acid of the saponified ethereal salt. It was partially distilled to remove alcohol and soluble oils. A small quantity of ammonia was always given off, possibly from the saponification of nitriles. Heusler found nitriles in coal tar.[1] The alcohol was assumed to be methyl alcohol.

(2) *Methyl Acetate (57°.3).*

The solutions of caustic soda containing the acids from the ethereal salts of the fractions 57.5°–61.5° and 61.5°–70°, were strongly acidified with dilute sulphuric acid and distilled. The crystallized silver salts prepared from the distillates gave the required percentage of silver for silver acetate.

From oil fraction 57.5°–61.5° :

0.6198 gram of the crystallized silver salt left, on ignition, 0.3983 gram silver.

	Calculated for $C_2H_3O_2Ag$.	Found.
Ag	64.66	64.26

From oil fraction 61.5°–70°.

First fractional precipitation :

0.8498 gram of the crystallized silver salt left, on ignition, 0.5435 gram silver.

[1] Ber. d. chem. Ges., **30**, 2743.

Fourth fractional precipitation:

0.8833 gram of the crystallized silver salt left 0.5661 gram silver.

	Calculated for $C_2H_3O_2Ag$.	Found. I.	IV.
Ag	64.66	63.96	64.09

Qualitative tests with iron and aluminium salts confirmed the presence of acetic acid.

Methyl acetate was first recognized in wood spirit by Völkel.[1] Together with methyl formate, which was first detected by him, it was later identified in crude wood spirits by Mabery.[2]

(3) *Methyl Propionate* (79°.5).

The acid distillate from fraction 70°–80° separated into two layers when treated with calcium chloride. The upper oily layer of fatty acid was lost. The acid in solution in the lower layer was distilled and the silver salt prepared from it.

First fractional precipitation:

0.3762 gram of the crystallized silver salt left, on ignition, 0.2262 gram silver.

Fifth fractional precipitation:

0.4556 gram of the crystallized silver salt gave 0.2745 gram silver.

	Calculated for $C_3H_5O_2Ag$.	Found. I.	V.
Ag	59.67	60.13	60.25

While propionic acid has been separated from wood vinegar, methyl propionate has not before been detected in any distillation-products of wood.

(4) *Methyl-n-butyrate* (102°.3).

The fatty acids from the fractions above 80° were distilled from the acidified soda solution with steam. The clear acid distillate from fraction 95°–105° was treated with calcium chloride, and the oily layer separated. It had the disagreeable odor of the higher fatty acids. After dehydrating with calcium chloride, it distilled almost completely at 157° to 162°.

[1] Ann. Chem. (Liebig), **86**, 66.

[2] This JOURNAL, **5**, 256.

The acid, separated in the same way from fraction 105°–110°, distilled at 157° to 162° also, and was mixed with the above. The silver salt of the acid, crystallizing in needles, gave the analysis for silver butyrate.

0.5612 gram of the crystallized silver salt gave, on ignition, 0.3105 gram silver.

	Calculated for $C_4H_7O_2Ag$.	Found.
Ag	55.38	55.33

The acid separated in a similar way from fraction 110°–115° distilled from 158° to 167°. From that portion boiling at 162° to 163° the crystalline silver salt was prepared and analyzed.

0.5658 gram of the silver salt left, on ignition, 0.3116 gram silver. Per cent Ag = 55.07.

Part of the acid 157°–162° was converted into the calcium salt, and the solution partially evaporated in the cold over sulphuric acid. On heating, a copious crystalline precipitate separated, showing the presence of normal butyric acid.

A test was made for isobutyric acid in the acid boiling at 157° to 162°, the method of Victor Meyer[1] being used with a slight modification. Thirty grams acid were oxidized with an alkaline solution of potassium permanganate, the filtered liquid treated with an excess of hydrochloric acid, and neutralized with chalk, then 2 or 3 drops of ammonia added. The crystals obtained by partial evaporation of the filtered solution were decomposed with dilute hydrochloric acid, and the solution extracted with ether. The ether was evaporated, and the residue, placed in a bell-jar, over sulphuric acid, crystallized in long needles. These were so small in quantity—much less than 0.1 gram—and so deliquescent, that a melting-point determination was not made. The crystals were probably of oxyisobutyric acid. Isobutyric acid yields oxyisobutyric acid when treated as above, which is a deliquescent substance and melts at 78° to 79°. Methyl isobutyrate, if present at all, is present in minute quantity. Krämer and Grodzki tried in vain to isolate isobutyric acid from wood vinegar by fractional distillation, etc., but obtained no indications of it.

Methyl butyrate has not before been detected in wood oil, or any other distillation-product of wood.

[1] Ber. d. chem. Ges., 30, 2525. See also criticism of Erlenmeyer: *Ibid.*, 30, 2956.

(5) *Esters of Unsaturated Acids.*

The acid from fraction 115°–120° became milky when distilled. The insoluble acid was separated; the remainder was neutralized, evaporated to dryness, and distilled with sulphuric acid. The clear distillate decolorized bromine, indicating unsaturated acids.

α-Crotonic acid and β-crotonic acid have been separated from wood vinegar by Krämer and Grodzki,[1] which renders probable the presence of their methyl esters in wood oil. Methyl α-crotonate boils at 120°.7, methyl β-crotonate probably at 114° to 116°.

(6) *Methyl Valerate (127°.3).*

The distillate from each fraction above 120° had an insoluble acid floating on it. The acid was separated, dried, and distilled. The acid from fraction 120°–130° distilled mainly from 178° to 182°. Its crystallized silver salt was analyzed.

0.5868 gram silver salt left, on ignition, 0.3047 gram silver.

	Calculated for $C_5H_9O_2Ag$.	Found.
Ag	51.67	51.94

The silver salt from the acid from fraction 130°–135°, boiling at 184° to 188°, also gave results for silver valerate.

First precipitation:

0.3892 gram of the crystallized silver salt left, on ignition, 0.2010 gram silver.

Fifth precipitation:

0.5302 gram of the crystallized silver salt gave, on ignition, 0.2745 gram silver.

	Calculated for $C_5H_9O_2Ag$.	Found.	
		I.	V.
Ag	51.67	51.67	51.77

The calcium and zinc salts of the acid boiling at 184° to 188° were more soluble in cold than in hot water, indicating normal valeric acid. Methyl valerate has not before been detected in any products of the distillation of wood.

(7) *Esters of Other Acids.*

The acid which floated on the surface of the distillate from

[1] Ber. d. chem. Ges., **11**, 1356.

fraction 135°–140° distilled at 189° to 194°, and analysis of its silver salt pointed to the presence of esters of organic acids with a higher molecular weight than valeric acid.

0.5213 gram of the crystallized silver salt left, on ignition, 0.2654 gram silver.

	Calculated for $C_5H_9O_2Ag$.	Calculated for $C_6H_{11}O_2Ag$.	Found.
Ag	51.67	48.43	50.91

Besides the volatile acids already described, the caustic soda solutions contained a small quantity of a very dark acid, which remained suspended in the acidified liquid after the other had been distilled off.

IV. OTHER KETONES.

The oils undissolved by the sodium hydroxide were dried and fractionated. The distillates reacted with phenylhydrazine, showing keto bodies still present. Phenylhydrazine was added to all the fractions above 85°, when action took place with evolution of heat and separation of water. After standing over night the excess of phenylhydrazine was removed with acetic acid, and the uncombined oil distilled with steam. Treatment with phenylhydrazine, etc., was repeated. The loss of the oil treated with sodium hydroxide in this operation averaged 24 per cent, greatest with fraction 105°–110°, least with fraction 135°–140°, with another maximum at fraction 115°–135°.

The phenylhydrazine compound remaining in the flask after the oil had been distilled was decomposed with concentrated hydrochloric acid, and the ketone distilled with steam. The distillate was unexpectedly small. It united in part with acid sodium sulphite. That which did not unite was dried with calcium chloride and distilled. It had the agreeable odor of ketones.

Ketone from fraction 85°–105° distilled for the most part at 98° to 101°, probably being diethylketone (103°).

Ketone from fraction 115°–135° distilled mostly at 118° to 122°.

Ketone from fraction 135°–140° distilled all the way from 130° to 140°.

The quantity of these distillates was not sufficiently large to justify further examination.

V. ABSENCE OF ALCOHOLS AND PYRIDINES.

After the removal of ketones from a wood spirit residue, Wislicenus and Looft[1] had left a liquid which reacted readily with acetic anhydride and acetyl chloride, and contained alcohols and pyridines. It was natural to suppose that the wood oil under investigation would have some resemblance to the product just named, and that the residue left after ethereal salts and ketones had been removed would contain alcohols and pyridines. Such was not the case, however. The residue did not react with phosphorus trichloride or with acetyl chloride, nor was there any indication of pyridines at any stage of the investigation, not even the odor. Other facts showed clearly that the wood oil under investigation differed materially from the wood spirit residue examined by the investigators named. Whether this difference is due to the method of distillation of the wood, or to the one being a "wood oil" from crude wood spirits, and the other a "wood oil" from wood tar, is an open question, but I am more inclined to the latter opinion.

VI. METHYLFURANE—DIMETHYLACETAL.

Atterberg[2] isolated a body C_5H_6O from the tar of *Pinus sylvestris*, which he recognized to be methylfurane. He named it sylvane. C. Harries[3] has recently separated the same body from beech-wood tar. The residue left from the tar boiling below 70°, after washing with sodium bisulphite and with caustic soda, fractional distillation and purification with sodium, yielded a chief fraction boiling at 65°, which proved to be almost pure sylvane. It was hydrolyzed to the aldehyde of levulinic acid, which showed it to be α-methylfurane.

$$\begin{array}{l} CH{=}C.CH_3 \\ | \quad >O \\ CH{=}CH \end{array} + H_2O = \begin{array}{l} CH_2{-}COCH_3 \\ | \\ CH_2{-}CHO \end{array}$$

[1] Ann. Chem. (Liebig), **275**, 366.
[2] Ber. d. chem. Ges., **13**, 879.
[3] *Ibid.*, **31**, 37.

Sylvane was present in the wood oil under investigation. The fraction 64°–70°, which had not been subjected to the action of phenylhydrazine, was treated with sodium and distilled after action had ceased. The colorless distillate soon became colored in the air. Heated with dilute hydrochloric acid in a sealed tube it formed a heavy oil, which gave the pyrrol reaction.

Proceeding in the manner described above—that is, treating with sodium bisulphite, sodium, etc., Roscoe and Dancer[1] isolated a compound with almost the same boiling-point (63°) as sylvane, from crude wood spirits, which, from analysis and the vapor density, they decided to be dimethylacetal. Considering that aldehydes and methyl alcohols come together at a high temperature during the distillation of wood, one might expect to find dimethylacetal as well as derivatives of higher aldehydes. Krämer and Grodzki state that dimethylacetal is a constant constituent of crude wood spirits. Mabery was unable to detect it in the crude wood spirits examined by him. Dimethylacetal might easily be present in the sylvane from wood tar, but a test proved that the one under investigation contained none.

Eleven cc. sylvane were poured through the tube of a condenser upon phosphorus iodide (from 44 grams iodine and 8 grams phosphorus). Reaction took place with evolution of heat. After heating for five minutes on the water-bath, the condenser was turned down, and an attempt made to distil off the product, but not a single drop came over, even after heating for half an hour. Dimethylacetal would have produced methyl iodide, volatile at 45°.

VII. OTHER FURANES.

Paal and Dietrich[2] have pointed out that very dilute aqueous hydrochloric acid at 170° hydrolyzes dimethylfurane to acetonylacetone:

$$\begin{matrix} CH{=}C{-}CH_3 \\ | \quad >O \\ CH{=}C{-}CH_3 \end{matrix} + H_2O = \begin{matrix} CH_3{-}CO{-}CH_3 \\ | \\ CH_2{-}CO{-}CH_3 \end{matrix}.$$

[1] Ann. Chem. (Liebig), **132**, 240.
[2] Ber. d. chem. Ges., **20**, 1085.

E. Fischer and Laycock[1] applied this method to the examination of a sugar oil. The fraction boiling about 94°, heated six hours at 170°, in a sealed tube with dilute hydrochloric acid, allowed acetonylacetone to be salted out with potassium carbonate from the acid solution; later Laycock[2] examined the oil boiling at about 115°, and obtained methylacetonylacetone. In the former investigation, Fischer and Laycock applied the method to a wood tar,[3] also. They say, "From the fraction 85°–100° by decomposition with dilute hydrochloric acid, we obtained a diketone which, in all probability is acetonylacetone. The fraction 100°–120°, treated in the same manner, gave a ketone which, from the analysis and the melting-point of the phenylhydrazine compound, seems to be the next homologue of acetonylacetone." This proves that dimethylfurane and trimethylfurane are present in the wood tar.

The oil unacted on by phenylhydrazine was dried and distilled. All aldehydes, ketones, and ethereal salts had now been removed. The distillates, colorless when fresh, rapidly become colored, assuming a yellow or dark-yellow color. A preliminary experiment, heating samples of the oil in sealed tubes with dilute hydrochloric acid, showed the presence of furanes, as the oil salted out by potassium carbonate from the hydrochloric acid solution gave the pyrrol reaction. As considerable quantities of material were to be treated with hydrochloric acid to remove furanes, heating in sealed tubes with dilute hydrochloric acid did not commend itself. It was found that the furane could be hydrolyzed by strong hydrochloric acid in the cold, with satisfactory results. The oil was shaken for fifteen hours with hydrochloric acid (2 vols. HCl, 1.175 sp. gr., to 1 vol. H_2O), on the shaker used for hydrolyzing the ethereal salts. The acid solution was neutralized with sodium carbonate, and the ketone in it salted out with potassium carbonate. The loss in volume of the oil was considered to represent the relative quantity of furanes hydrolyzed; it decreased regularly, and in the oils freed from

[1] Ber. d. chem. Ges., **22**, 101.
[2] *Ibid.*, **10**, 1358.
[3] Ann. Chem. (Liebig), **258**, 230.

ketones and ethereal salts, varied from 66 per cent in fraction 85°–95° to 10 per cent in 130°–140°.

(1) *Dimethylfurane.*

Fractions 85°–95° and 95°–105° together yielded about 14 cc. ketone boiling at 187° to 193°, mainly at 191° to 192°. Eleven grams of this with 12 grams hydroxylamine and 13 grams sodium carbonate in 30 cc. water, gave a precipitate of 10 grams oxime. Recrystallized from water, its melting-point (134°), and analysis proved it to be the dioxime of acetonylacetone.

0.3556 gram substance yielded 55.21 cc. nitrogen under standard conditions.

	Calculated for $CH_3C.(N.OH)C_2H_4C.(N.OH)CH_3$.	Found.
N	19.37	19.48

Acetonylacetone was produced by the hydrolysis of dimethylfurane.

(2) *Trimethylfurane.*

The ketone produced by the hydrolysis of fraction 115°–130° distilled at 199° to 202°, mainly at 200° to 201°. The dioxime prepared as above melted at 128° to 129° after it was recrystallized from water. Analysis and melting-point confirmed the belief that it was the dioxime of methylacetonylacetone.

0.1832 gram substance yielded 25.8 cc. nitrogen under standard conditions.

	Calculated for $C_7H_{12}(NOH)_2$.	Found.
N	17.72	17.67

Methylacetonylacetone was produced by the hydrolysis of trimethylfurane.

VIII. UNSATURATED COMPOUNDS.

The dark-colored oils remaining undissolved after treatment with hydrochloric acid were dried with potassium carbonate and distilled. Addition of hydrochloric acid had taken place, and perhaps condensation reactions also, as they contained substances which boiled much higher than the original oil. Each fraction was distilled to a temperature 10° to 15° above

its previous boiling-point. The distillates are described below. The residue varied from 56 per cent of the fraction 85°–95° to 4 per cent of fraction 140°–145°, showing that the quantity of compounds affected by hydrochloric acid decreases with the boiling-point. The boiling-point of the residue from fraction 85°–95° went above the range of the thermometer. The residues gave a heavy precipitate when boiled with alcoholic silver nitrate, showing the addition of hydrochloric acid. Unsaturated compounds which add hydrochloric acid are present in quantities that decrease as the boiling-point rises.

The distillates were subjected to three fractional distillations. They accumulated in the fractions boiling at 108° to 112° and 137° to 140°.

Concentrated sulphuric acid acted slightly on all the fractions, becoming yellow, and more decidedly on fraction 115°–118°. In the latter case oil and acid both became red-brown. Bromine in carbon disulphide was decolorized rapidly by all the fractions, with no hydrochloric acid fumes evolved at first; after standing a short time, hydrobromic acid was given off, the liquid became brown, and a brown oil separated. These reactions evidently indicate unsaturated compounds. The fractions 108°–112° and 137°–140° consisted for the most part of aromatic hydrocarbons, but they contained a body which gave with nitric acid a bright-red coloration, which quickly disappeared.

IX. AROMATIC HYDROCARBONS.

Toluene and metaxylene, cumene and cymene have been detected in wood tar. The chief fractions 108°–112° and 137°–140° correspond to the first two hydrocarbons.

Twenty grams of fractions 108°–112° treated with nitric and sulphuric acids yielded 30 grams of the nitro compound. This crystallized from alcohol in long needles, which melted at 70°, and is dinitrotoluene. At least 75 per cent of fraction 108°–112° was toluene.

Twenty grams of fraction 137°–140° yielded 30 grams of a nitro compound, difficultly soluble in alcohol, and crystallizing from benzene in needles which melted at 180°.5 (uncorr.), and is trinitro-*m*-xylene. At least 65 per cent of fraction 137°–145° was *m*-xylene.

X. SUMMARY OF RESULTS.

The following is a summary of the results reached in the first part of this investigation :

Wood oil.

Removed by Sodium Bisulphite :

Aldehydes.

Valeric aldehyde.

Ketones.

Acetone.

Methylethylketone.

Methylpropylketone.

Methylbutylketone.

Adipic ketone.

Residue.

Removed by Caustic Soda :

Nitriles.

Ethereal salts.

Methyl acetate.

Methyl propionate.

Methyl *n*-butyrate.

Methyl *n*-valerate.

Esters of unsaturated acids.

Residue.

Sylvane.

Removed by Phenylhydrazine :

Ketones.

Diethylketone.

Residue.

Removed by Hydrochloric Acid :

Furanes.

Dimethylfurane.

Trimethylfurane.

Residue.

Distillation :

Volatile :

Unsaturated compounds.

Aromatic hydrocarbons.

Toluene.

m-Xylene.

Residue.

Hydrochloric acid addition-products.
Polymerized compounds.

PART II.

INVESTIGATION OF THE WOOD OIL BOILING ABOVE 140°.

As shown in the preceding pages, the wood-oil boiling below 140° consists of an homologous series of aldehydes, ketones, furanes, ethereal salts, aromatic hydrocarbons, and unsaturated compounds whose nature was not determined. The wood oil boiling above 140° has been little investigated. Several ketones, indications of higher alcohols, cumene, cymene, furfural, methylfurfural, and methylpyridine have been found in it from time to time, but the composition of the greater portion of the oil is still unknown. It was hoped to extend the homologous series found in the lower-boiling oils into the higher fractions, and perhaps find new series. The investigation was not carried far, however.

The oil left after distilling off the portion boiling below 140°, about 7.5 liters, was fractionated three times without a Hempel tube. The distillation was attended with slight decomposition and continuous elimination of a small quantity of water, especially noticeable when the distillation was discontinued and renewed. Krämer and Grodzki observed the same phenomenon. The decomposition became very marked at 195° to 200°, and the first distillation was stopped at 200°. The two succeeding fractionations were carried to 210°. Only one chief fraction, boiling at 165° to 170°, appeared, little different in size, however, from those boiling at 155° to 160°, 160° to 165°, and 170° to 175°. These four fractions contained 45 per cent of the distillate between 140° and 210°. Other fractions diminished regularly on each side.

I. ALDEHYDES—KETONES.

Fractions boiling over 180° gave no precipitate with sodium bisulphite, and with the lower boiling fractions the quantity was small. The distillates from the sulphite compounds, decomposed with sodium carbonate, gave the silver mirror, but the quantity of aldehydes was too small to allow their identi-

fication. Fraction 155°–160° and the distillate from the sulphite compound from fraction 150°–155° gave the red color with aniline acetate, which indicates furfural. Not sufficient of it was present to respond to a more decisive test.

The dried ketones were once fractionated. The chief fraction boiled at 145° to 150°, with small quantities boiling up to 185°. Pimelic ketone or cyclohexanone (153°), separated by Looft from crude wood spirits residue, was expected to be present. It yields adipic acid on oxidation with nitric acid. Ketone fraction 150°–155 oxidized with nitric acid 1.2 sp. gr. left a solid acid on evaporation, which crystallized from water in thin leaves melting at 95°. Adipic acid melts at 148°. There was not sufficient of the acid for further examination.

Looft separated an unsaturated ketone, β-methylketopentamethenylene or methylcyclopentanone from the residue of crude wood spirits by means of the oxime. It boils at 157°, and unites easily with acid sodium sulphite to form a compound very soluble in water, not decomposed by alkalies or alkaline carbonates, but decomposed by hydrochloric acid. This ketone appears to be absent from the wood oil here examined, or, if present, only in minute quantities. To test for it, the sulphite residue and compound from the fractions 145°–150° and 150°–155° were distilled with sodium carbonate to remove all other ketones, then distilled with a large excess of hydrochloric acid. A few drops of oil came over, with the odor of fatty acids, and almost all of it dissolved in sodium carbonate.

II. ETHEREAL SALTS—CREOSOTE.

Like the ketones, ethereal salts were present in very small quantity. They were saponified as in Part I, and the loss of oil at first considered to represent the quantity of ethereal salts removed, but most of the loss in the fractions boiling above 150° was later found due to the presence of creosote, not ethereal salts. The percentage of loss in the oil washed with sulphite solution decreased from 18 per cent in fraction 135°–140° to 4 per cent in fraction 145°–150°, then increased regularly np to 45 per cent in fraction 205°–210°. The increase was

caused by increasing amounts of creosote. The acids separated from the solution of caustic soda were dried and once fractionated. The distillates were found to contain phenols. They were dissolved, in three portions, in a solution of caustic soda; the phenols liberated by saturating with carbon dioxide, separated, and the solution extracted with ether. The phenols were not further examined.

The purified acids were liberated with sulphuric acid, separated, dried, and once fractionated. All the fractions were small. The distillates were colorless up to 210°, then slightly yellow, and all had the odor of the monobasic fatty acids. A small quantity of solid acid separated from fractions 225°–235°, which was not further examined. The largest fraction was the one boiling from 195° to 200°. Its silver salt was prepared and analyzed.

0.3777 gram of the silver salt left, on ignition, 0.1892 gram silver.

	Calculated for $C_5H_9O_2.Ag$.	$C_6H_{11}O_2Ag$.	Found.
Ag	51.67	48.43	50.09

The acid was plainly a mixture. A little potassium carbonate was added to it, and the acid distilled off. The silver salt from the residue approached the composition of silver valerate. One would expect the acid of higher molecular weight to remain combined with the potash but this was not the case.

0.9509 gram of the silver salt left, on ignition, 0.4872 gram Ag.

	Calculated for $C_5H_9O_2Ag$.	Found.
Ag	51.67	51.23

The acid is a mixture of valeric and caproic acids.

Methyl *n*-valerate was found in the oil which distilled below 140°. It appears that methyl caproate is also present.

Fraction 220°–225° of the acid also appears to be a mixture. The silver salt gave the following analysis:

0.5915 gram silver salt left, on ignition, 0.2760 gram silver.

	Calculated for $C_6H_{11}O_2Ag$.	$C_7H_{13}O_2Ag$.	Found.
Ag	48.43	45.57	46.66

The acid is perhaps a mixture of caproic and heptoic acids, and methyl heptoate is present in wood oil. Small quantities of the fatty acids distilled above 225°, but they could not be examined. According to this, acids of higher molecular weight than caproic acid will be found in wood vinegar.

III. FURANES— UNSATURATED COMPOUNDS.

A very small percentage of the oil consists of furanes. Shaken with hydrochloric acid (fractions 150°–155°, 160°–165°, 170°–175° tried), it becomes very dark and a small part dissolves. Oils could be salted out from the solutions, which appear to be diketones. Furanes higher than trimethylfuranes are present, and make up a very small fraction of the oil.

The very dark oil separated from the concentrated hydrochloric acid had undergone a change, by addition of hydrochloric acid, and perhaps polymerization. Fraction 150°–155°, treated with hydrochloric acid and dried with potassium carbonate, when distilled, began to decompose with formation of hydrochloric acid when the temperature passed beyond 155°. That portion of it which distilled at 175° to 180°, after having been well washed with sodium carbonate and water, gave a copious precipitate of silver chloride when heated with alcoholic silver nitrate. The compounds which take up hydrochloric acid or are polymerized or decomposed by it, make up a considerable proportion of the wood oil.

IV. PHENOL ETHERS.

Since, in the distillation of wood, phenols and methyl alcohol come together at high temperatures, and at th emoment of formation one might reasonably expect to find neutral phenol ethers in the products. Wood-tar creosote consists of monophenols and the acid methyl ethers of di- and tri-acid phenols, which also would lead one to look for neutral methyl ethers in the distillation-products of wood.

Forty cc. of fraction 150°–155°, previously treated with hydrochloric acid, and forty cc. of fraction 175°–180°, were heated with 30 cc. concentrated hydrochloric acid in sealed tubes for five and a half hours at 175° to 180°. On opening the cold

tubes gas escaped with effervescence, which burned with a beautiful dark-green flame (methyl chloride). The acid solutions were separated, made alkaline with potassium carbonate, and distilled with steam. Both distillates gave precipitates with bromine water, but neither would give the color reaction with ferric chloride. Distillate from fraction 175°–180°, however, had the unmistakable odor of cresol, and I therefore, consider that this test shows the probable presence of minute quantities of neutral phenol ethers in the wood oil.

Tiemann and Kopp[1] separated an indifferent oil from wood tar creosote, which, from determination of the vapor-density of the different fractions, they decided to be a mixture of neutral phenol ethers with hydrocarbons. Their oil boiled above 205°; and methylphenyl ether (155°) and the methyl cresol ethers, could not have been contained in it.

V. CERTAIN REACTIONS.

The work just described shows that the wood oil boiling above 140° contains creosote, and very small percentages of aldehydes, ketones, furanes, ethereal salts, and phenol ethers. The remainder of the oil contains, in all probability, the aromatic hydrocarbons cumene and cymene, as well as large quantities of unsaturated compounds and other bodies of unknown nature. It was not thought profitable to separate the aromatic hydrocarbons, and investigation of the unknown portion was not inviting, considering the time and quantity of material then available. Beyond certain reactions which afford possible points of attack, the research was not carried further.

Acetyl chloride and phosphorus trichloride gave no indications of alcohols. Potassium permanganate oxidized the oils with great energy, but not completely.

Concentrated sulphuric acid dissolves part of the oil with heat, and the acid becomes very dark. The undissolved oil has an aromatic odor and consists, for the most part, of aromatic hydrocarbons. The aromatic hydrocarbons were separated by previous investigators in this manner. When the acid is poured into water, a dark-brown oil separates, which

[1] Ber. d. chem. Ges., 14, 2005.

possesses an agreeable odor. An oil separated by Völckel[1] in a similar manner from beech-wood tar gave on analysis (from tar fraction 140°–150°) :

C	75.11
H	10.38
O	14.51

The oil had been purified by distillation with steam.

Bromine is absorbed with the greatest avidity. If the product is distilled with water vapor, an oil lighter than water passes over, then an oil heavier than water, and a black tar remains behind. If an attempt is made to distil the oil heavier than water by itself, it decomposes.

Glacial acetic acid allows the wood oil to be separated into two portions, one soluble, the other insoluble or soluble with great difficulty. For example, 100 grams glacial acetic acid dissolved 6 cc. from 50 cc. of the fraction 160°–165°, plus 40 cc. from 380 cc. of the same fraction. The acetic acid solution took up bromine without evolution of hydrobromic acid, and a heavy oil separated when the product was poured into water. The product was distilled with steam ; a heavy oil first passed over, then a yellow solid crystallizing in long needles comes over very slowly. There was not enough of the latter to recrystallize. The oil turned red when heated above 100° and gave off acid fumes. It then quickly became black, and began to distil at 180°, with considerable decomposition.

The acetic acid solution yields a solid, crystalline precipitate when shaken with water and potassium nitrite.

SUMMARY AND CONCLUSIONS.

The following are the results of this research :

(1) The wood oil examined is a mixture of homologous series of different classes of compounds.

(2) It probably contains the series of aldehydes $C_nH_{2n}O$, corresponding to the series of saturated acids $C_nH_{2n}O_2$, found in wood vinegar, which goes up to and includes caproic acid. The quantity of aldehydes is so small that only one could be positively identified, valeric aldehyde. Acetic aldehyde and propionic aldehyde have been found in wood oil by other in-

[1] Ann. Chem. (Liebig), **86**, 331.

vestigators, and these facts justify the first statement. It contains furfural in minute quantity.

(3) It contains the series of ketones $C_nH_{2n}O$, of which dimethylketone, methylethylketone, methylpropylketone, and probably methyl-*n*-butylketone and diethylketone have been detected.

(4) It contains the ring ketone, cyclopentanone, and other ring ketones.

(5) It contains no mesityl oxide nor methylcyclopentanone.

(6) It contains nitriles in minute quantity.

(7) It contains the methyl esters of the saturated acids, $C_nH_{2n}O_2$, found in wood vinegar, including methyl acetate, methyl propionate, methyl *n*-butyrate, methyl *n*-valerate, very probably methyl caproate, and methyl heptoate and possibly methyl isobutyrate. The acid corresponding to methyl heptoate has not yet been found in wood vinegar. The percentage of ethereal salts decreases as their boiling-points rise, the lower-boiling ones being present in considerable quantity, the higher ones in very small quantity. One might conclude from this that the quantity of the corresponding acids in wood vinegar decreases with increase in boiling-point.

(8) It contains the esters of unsaturated acids.

(9) It contains methylfurane, and furanes which can be hydrolyzed by cold, strong hydrochloric acid to diketones. The furanes include dimethylfurane, trimethylfurane, and higher furanes.

(10) It contains no dimethylacetal, nor appreciable quantities of pyridines or alcohols.

(11) It contains compounds which take up hydrochloric acid and bromine, and are therefore unsaturated.

(12) It contains the aromatic hydrocarbons, toluene and xylene, and probably cumene and cymene.

(13) It contains creosote.

(14) It contains phenol ethers in minute quantity.

(15) The higher boiling oils, freed from ketones, aldehydes, ethereal salts, and creosote can be separated into two parts by glacial acetic acid, the one soluble in that substance, the other insoluble. Both absorb bromine readily.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXVII.—ON TRIPHENYLCHLORMETHANE.

By James F. Norris and Warren W. Sanders.

In a study of the application of the Friedel and Crafts reaction to halogen compounds in which the halogen is not joined to carbon, an account of which will be given in a subsequent paper, it was found that under certain conditions condensation-products could be isolated, the preparation of which, by the usual method of procedure, was impossible. For example, when phenyliodide dichloride and benzene were used, one of the chlorine atoms was replaced by phenyl and diphenyliodonium chloride was formed. As the method of carrying out the reaction is different from that which is usually employed in condensations with aluminium chloride, it seemed possible that a study of some carbon compounds under the conditions used in preparing the iodonium chloride, might lead to interesting results.

Carbon tetrachloride was first investigated. This reaction had been previously studied by Friedel and Crafts and by E. and O. Fischer with the result that triphenylmethane and not tetraphenylmethane was obtained. On account of this fact the study of this compound seemed of especial interest. As the result of the reaction we obtained triphenylchlormethane.

An account of this work was about to be sent to the editor of this Journal, when the paper by Gomberg,[1] describing the study of this reaction, appeared. Our results are essentially those of Gomberg, but the procedure used by us is somewhat different. The yield of the pure reaction-product which has been obtained is greater, and, further, we have succeeded in isolating a crystalline intermediate product containing aluminium, which has a bearing on the recently published explanation of the mechanism of the Friedel and Crafts reaction.

Gomberg[2] has also reported a study of the action of metals on triphenylchlormethane and has obtained an unusually interesting substance, which is considered to be the free radical

[1] J. Am. Chem. Soc., **22**, 752.

[2] *Ibid.*, **22**, 757.

triphenylmethyl, $(C_6H_5)_3C$—. He wishes to reserve this field for further work. As we have been working with triphenylchlormethane in this laboratory for about a year, with the view of preparing tetraphenylmethane from it, it seems advisable to give a preliminary account of the work that has been accomplished, and to describe briefly what is now in progress.

The method of carrying out the Friedel and Crafts reaction, which we have found to give excellent results, consists, in brief, in adding aluminium chloride to a mixture of the theoretical quantities of the halogen compound and the hydrocarbon dissolved in a comparatively large quantity of carbon disulphide, care being taken to prevent a rise in temperature during the reaction. The flask containing the mixture is placed in ice-water, which slowly comes to the room temperature. The reaction is allowed to proceed for from twelve to forty-eight hours. When carbon tetrachloride and benzene were brought together under these conditions, a reaction took place slowly, and at the end of a few hours a heavy, dark-brown oil had separated. At the end of three days' crystals were seen in the oil, which changed, on standing, into a solid mass of crystals cemented together by a dark, amorphous substance.

These crystals decomposed rapidly when brought into contact with the air. They were insoluble in benzene, carbon disulphide, carbon tetrachloride, and petroleum ether. They were decomposed by alcohol, ether, acetone, chloroform, and acetic acid, but were soluble in nitrobenzene without decomposition. The compound was recrystallized from a mixture of nitrobenzene and carbon disulphide, and was obtained in the form of brown monoclinic prisms, terminated by basal planes, and modified by orthopinacoids. In one experiment crystals one-half inch in length were formed. The compound was found on analysis to have the composition represented by the formula $Al_2Cl_6.2(C_6H_5)_3C.Cl$.

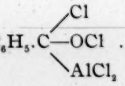
When these crystals, or better the heavy oil from which the crystals separate, are treated with ice, the compound is broken up, and triphenylchlormethane is formed. By proceeding with care, 97 per cent of the theoretical yield was obtained. Hemilian,[1] who prepared the chloride from triphenylcarbinol

[1] Ber. d. chem. Ges., 7, 1203.

and phosphorus pentachloride, gives 105°–115° as its melting-point. We prepared samples of the chloride, by crystallizing it from a mixture of carbon disulphide and petroleum ether, which melted at 108°–111°. Recrystallization did not change the melting-point. Gomberg found that the substance melts usually at 108° to 112°. As triphenylchlormethane is readily converted into tripheuylcarbinol by the action of water, the preparation of the carbinol is best effected by this reaction.

The formation of an addition-product of aluminum chloride and triphenylchlormethane is in accord with the explanation of the mechanism of the Friedel and Crafts reaction which has been put forward by Boeseken.[1] In studying the condensation of acid chlorides and hydrocarbons by this reaction it was found that a compound of the organic and inorganic chloride is first formed; that this compound reacts with the hydrocarbon with the evolution of hydrogen chloride; that an addition-product of the resulting ketone and aluminum chloride is then formed; and that, finally, this compound is broken down by water and the ketone is set free. In view of these facts an effort was made to prepare a compound of carbon tetrachloride and aluminum chloride to discover if the above explanation could be applied in full to this particular case. No such compound could be isolated.

In a recent paper Kronberg[2] has suggested that the formation of addition-products of aluminum chloride and acid chlorides is due to the fact that acid chlorides contain a carbonyl group. The structure assigned to the compound containing benzoyl chloride, for example, is as follows:



The nature of the compound containing triphenylchlormethane cannot be explained in this way. In view of this and the fact that Kohler[3] has shown that these addition-products of acid chlorides and aluminium chloride have double the molecular

[1] Rec. trav. chim. Pays-Bas., **19**, 19.
[2] J. prakt. Chem. [2], **61**, 494.
[3] This JOURNAL, **24**, 385.

weight which has been assigned to them, for example the above compound has the formula $Al_2Cl_6.2C_6H_5COCl$, it seems that the suggestion of Kronberg does not explain the facts. The structure of the compound of aluminium chloride and triphenylchlormethane is best explained by giving to it a formula analogous to those proposed by Remsen[1] for the inorganic double chlorides. The compound is of interest as it is the first addition-product of aluminium chloride and an alkyl halide that has been described.

The isolation of a compound of aluminium chloride and triphenylchlormethane furnishes what appears to be a probable explanation of the non-formation of tetraphenylmethane from carbon tetrachloride. The double compound is readily formed from its constituents and is insoluble in benzene and carbon disulphide. Consequently, during the course of the reaction, as soon as three chlorine atoms have been replaced by phenyl groups, addition takes place, and the compound is precipitated and thus removed from further action. The opinion has been put forward that the non-formation of tetraphenylmethane by this reaction is due to the fact that there is not sufficient room for four phenyl radicals to be grouped about one carbon atom. It seems probable, in view of the facts as now known, that this stereochemical explanation is gratuitous.

Some time ago Gomberg[2] described a method of preparing tetraphenylmethane. As less than 0.5 gram of the substance was obtained in the first investigation, and a careful revision of the work[3] did not lead to a better yield, it seemed of importance to attempt to prepare the hydrocarbon by another reaction. A number of chemists have endeavored to obtain this compound. Most of the usual synthetical methods have been studied, but in no case was tetraphenylmethane obtained. As we had worked out a method of preparing triphenylchlormethane readily, we attempted to condense it with brombenzene by means of sodium. This application of the Fittig synthesis—apparently the most direct method of preparing the hydrocarbon—had not been studied, no doubt for the reason

[1] This JOURNAL, **11**, 291.
[2] Ber. d. chem. Ges., **30**, 2043.
[3] J. Am. Chem. Soc., **20**, 773.

that Elbs[1] and others had found that triphenylbrommethane is not acted upon by sodium. Anschütz[2] endeavored to condense triphenylbrommethane and benzyl chloride and obtained as the result of the reaction dibenzyl and unchanged triphenylbrommethane. We, nevertheless, studied this reaction, thinking that with brombenzene a condensation might result, as it is known that a mixture of a halogen derivative of an aromatic hydrocarbon and an alkyl halide condense more readily than two alkyl halides. In other words, that a Fittig synthesis is possible at times when a Wurtz synthesis fails. In the experiment of Anschütz two halogen derivatives of methane were used.

As the formation of three compounds is possible in a synthesis of this kind involving two different halogen compounds, we subjected triphenylchlormethane, dissolved in ether, to the action of sodium under the same conditions of concentration and temperature which were used when brombenzene was present, in order to make ourselves sure that hexaphenylethane was not formed. The solution of the halogen compound was allowed to stand two weeks in contact with sodium, and finally was heated to boiling for an hour. As no change was apparent, the ethereal solution was decanted and evaporated to crystallization. The compound obtained was shown to be triphenylchlormethane.

To a mixture of triphenylchlormethane, ether, and sodium, identical with the above and prepared at the same time from the same reagents, brombenzene was added. In this case a reaction took place. The ether soon assumed a light-brown color and a powder separated. The reaction was complete in about three days. The ethereal solution was decanted from the insoluble reaction mixture, and yielded, on evaporation, diphenyl. The amount obtained corresponded to about one-half of the brombenzene used in the experiment. The reaction-product which separated from the ether was found to be a mixture. One of the constituents of this mixture was obtained in crystalline condition and was analyzed. The crystals were shown not to contain halogen, yet on analysis the

[1] Ber. d. chem. Ges., **17**, 700.
[2] Ann. Chem. (Liebig), **235**, 226.

carbon and hydrogen did not add up to 100 per cent. We made a number of analyses, thinking that our work was at fault, but repeated effort gave practically the same results. This compound resembles closely in melting-point, chemical composition, and solubility the substance obtained by Gomberg when triphenylchlormethane was treated with zinc. Gomberg expected the formation of a hydrocarbon, but, as in our case, repeated analyses finally proved that the substance was an oxygen compound. Gomberg has come to the conclusion that the substance is a peroxide of the formula

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3,$$

and that it is the result of the action of oxygen on the free radical $(C_6H_5)_3C—$, which is first formed when triphenylchlormethane is treated with zinc. The compound isolated by us resembles closely this peroxide, but further work is necessary before the identity of the two substances can be established.

We had reached this stage in our work, when the close of the school-year made it necessary to postpone the further investigation of the subject. We propose to study carefully the action of sodium on a mixture of triphenylchlormethane and brombenzene, and to isolate if possible the other products of the reaction The work which is being carried on at present, and which is to be continued, has for its ultimate aim the preparation of tetraphenylmethane. While it has a bearing on the work of Gomberg, who has reserved this field, it is in itself quite distinct. We discovered that an oxygen compound was formed as the result of the action of sodium on a mixture of triphenylchlormethane and brombenzene, and the work which is now in progress was planned in order to find an explanation of the formation of this substance. We propose to investigate the action of sodium on ethereal solutions of triphenylchlormethane of varying concentrations. Experiments with a number of alkyl halides have shown that the concentration of the ethereal solutions of the halides is an important factor in the Wurtz synthesis. Preliminary experiments seem to indicate that with triphenylchlormethane the concentration determines whether a reaction takes place or not.

The action of sodium on a mixture of carbon tetrachloride and brombenzene is also being studied. This reaction it is hoped will yield tetraphenylmethane. The fact that Polis[1] obtained an almost theoretical yield of silicon tetraphenyl by an analogous reaction in which silicon tetrachloride was used, makes the study of carbon tetrachloride under the same conditions of especial interest. We have found in the case of carbon tetrachloride, that a reaction takes place readily in benzene or ethereal solution. When ether is the solvent, the reaction-product separates in large quantities. The results of these experiments will be published later.

As the method of carrying out the Friedel and Crafts reaction which we have employed, has given such a good result with carbon tetrachloride, other halogen compounds will be studied in the same way. It seems probable that the reaction-products may be obtained more readily, and that better yields may result. On account of the fact that the preparation of triphenylmethane by this reaction from chloroform results in the formation of a number of side-products, from which the hydrocarbon is obtained in pure condition with difficulty, this reaction will be first investigated.

EXPERIMENTAL.

The following directions for the preparation of triphenylchlormethane were found to give excellent results. Twenty-five grams of carbon tetrachloride and 50 grams of benzene are dissolved in 100 cc. of carbon disulphide. The flask containing the mixture is placed in ice-water and after about five minutes 30 grams of aluminium chloride are added. The evolution of hydrogen chloride begins in a few minutes and continues for one and a half to two days. At the end of this time the mixture is poured upon ice and vigorously stirred. The carbon disulphide is separated from the mixture, which is extracted twice more with carbon disulphide. The combined extracts are united, filtered, and evaporated almost to dryness, care being taken to avoid the presence of moisture. The crystals of triphenylchlormethane which separate, are treated with the smallest quantity of petroleum ether which will dis-

[1] Ber. d. chem. Ges., **18**, 1541; **19**, 1013.

solve them. When the solution cools, the compound is obtained in the form of stout, radiating needles, at times one-half inch in length, which have a slight pink color. The product of this first crystallization usually melts at 100° to 102°. In order to obtain the compound in a high state of purity, it was dissolved in petroleum ether containing a small amount of carbon disulphide and boiled with dry bone-black. In this way colorless crystals were obtained. The melting-point was raised by this second crystallization to 105°–106°. When recrystallized a second time in the same way the compound melted at 108°–111°. Recrystallization did not change the melting-point. When great care was taken to get all of the triphenylchlormethane formed in the reaction a yield of 97 per cent was the result. Other experiments gave without special effort 79 and 83 per cent.

Triphenylchlormethane dissolves readily in carbon disulphide, benzene, carbon tetrachloride, chloroform, and ether. It is much less soluble in petroleum ether. The substance is readily decomposed by water, and is slowly converted into triphenylcarbinol by the moisture in the air.

When a mixture of carbon disulphide, carbon tetrachloride, aluminium chloride, and benzene, in the proportions given above, was allowed to stand about three days, crystals appeared in the dark-brown oil, which was the product of the reaction. This oil eventually changed into a mass of crystals, which were purified by recrystallization. A quantity of the impure substance was dissolved in nitrobenzene. To separate portions of this solution, carbon disulphide was added in varying quantities. The resulting mixtures were put aside in flasks, which were corked to prevent evaporation. After four days the solutions were examined, and in the flask which contained 2 parts of nitrobenzene and 3 parts of carbon disulphide, large, well-formed, dark-brown crystals were found. These crystals decomposed rapidly in the air. Hydrogen chloride was given off and a coating of aluminium hydroxide was formed. The compound began to decompose at 122° to 125°. In order to obtain the crystals in pure condition for analysis, they were removed, one by one, from the mixture from which they had been crystallized, and were quickly cov-

ered with nitrobenzene. They were then placed in successive mixtures of nitrobenzene and carbon disulphide, which contained less and less of the nitro compound. The crystals were finally washed with pure carbon disulphide and quickly dried between filter-paper. The aluminium was determined by heating with concentrated nitric acid a weighed sample of the substance and finally igniting. The chlorine was determined by the Carius method (Analysis II), and by heating the compound with water, filtering, and estimating the chlorine in the filtrate (Analysis III).

The results of the analyses follow :

I. 0.2918 gram substance gave 0.0368 gram Al_2O_3.
II. 0.3224 gram substance gave 0.4457 gram AgCl.
III. 0.2874 gram substance gave 0.3996 gram AgCl.

	Calculated for $Al_2Cl_6.2(C_6H_5)_3C.Cl$.	Found. I.	II.	III.
Al	6.60	6.68	....	....
Cl	34.63	....	34.43	34.40

The compound was heated with water and the triphenylcarbinol was filtered off and weighed. The amount obtained was 57.98 per cent instead of 63.02 per cent, the amount required by theory. This low result was shown to be due to the fact that the carbinol was volatile to some extent with the water that was driven off in drying it. Some crystals which were removed from the original reaction mixture before it had solidified, were analyzed without recrystallization, and were found to be quite pure.

BOSTON, MASS., November 12, 1900.

THE CONDUCTIVITIES OF SOME DOUBLE SALTS AS COMPARED WITH THE CONDUCTIVITIES OF MIXTURES OF THEIR CONSTITUENTS.

BY CHARLES F. LINDSAY.

Earlier investigations[1] in this laboratory have shown that the conductivities of solutions of double salts differ greatly from the sum of the conductivities of the constituents. These

[1] Jones and Mackay : This JOURNAL, **19**, 83; Jones and Ota : *Ibid.*, **22**, 5; Jones and Knight : *Ibid.*, **22**, 110.

differences are, in some cases, very large indeed, in the more concentrated solutions, and gradually become less and less as the dilution increases. The fact that the sum of the conductivities of the constituents is greater than the conductivity of the double salt, indicates that the double salt does not dissociate in solution in the same way as its constituents; *i. e.*, it does not break down into its constituents and then each of these dissociate as it would if alone in the solution.

The conclusion which has been reached is that double salts in concentrated solution dissociate to a greater or less extent as if they were salts of complex acids, and, then, as the dilution increases, the complex ion dissociates into the simplest ions. Since the differences found with the double chlorides, bromides and iodides are larger than with the double sulphates, an example will be taken from one of these classes to make the above point clear. Take the double bromide of barium and cadmium, $BaBr_2CdBr_2$. The conductivity of the double salt[1] at a volume of two is about thirty per cent less than the sum of the conductivities of the constituent bromides at this dilution. This difference rapidly diminishes with increase in dilution until at 100 liters it is about 8 per cent, and at 1,000 liters about 4 per cent. These results can be explained best by assuming that in the more concentrated solutions some of the double molecules are electrolytically dissociated thus:

$$BaBr_2CdBr_2 = \overset{+\,+}{Ba} + \overset{=}{CdBr_4},$$

While, with increase in dilution, the complex ion, $\overset{=}{CdBr_4}$, breaks down more and more into the simple ions,

$$\overset{+\,+}{Cd} + \overset{-}{Br} + \overset{-}{Br} + \overset{-}{Br} + \overset{-}{Br}.$$

At a dilution of 10,000 liters the salt is almost completely dissociated into its simplest ions.

The differences between the conductivity of the double salt and the sum of the conductivities of its constituents are considerably smaller for the double sulphates than for the double halides, but even with the double sulphates the differences are

[1] This JOURNAL, **22**, 132.

too large to be accounted for on the ground that each constituent would drive back the dissociation of the other. That this influence would come into play in all solutions which are not isohydric is well known, but it was shown that this would not account even for the cases where the smallest differences were found.

In connection with the above work some measurements had been made which indicated that the conductivity of a double salt is not exactly the same as the conductivity of a mixture of its constituents, having the same concentration as the double salt. This result, if true, would be so surprising that it seemed very desirable to investigate the question as thoroughly and carefully as possible. The work described in this paper was undertaken, then, to determine whether there is any difference between the conductivity of a double salt and the conductivity of a mixture of the constituents of the double salt having the same concentration. This investigation was extended to two double sulphates and one double chloride.

General Method of Work.

The double salt was prepared by weighing out the constituents as nearly as possible in the proportion in which they occur in the double salt in question, dissolving these and evaporating to crystallization. The double salt, which was always obtained in well-defined crystals, was dried by filter-paper, and when enough had been obtained for work the whole preparation was fairly sampled and carefully analyzed. In this way the purity of the double salt was established. A solution of the double salt was prepared having approximately the concentration desired, and the solution standardized by analysis. The more dilute solutions were prepared by suitably diluting this mother-solution in measuring flasks. In a number of cases the more dilute solutions were analyzed directly to avoid any possibility of error in making the dilutions. All the water used was prepared by the method of Jones and Mackay.[1] The preparation of solutions containing the mixture of the constituents of the double salt was more difficult. In most cases the following method was adopted: A solution

[1] This JOURNAL, 19, 91.

of approximately the desired concentration of each of the constituent salts, which had been very carefully purified, was prepared. Each solution was then standardized gravimetrically. These standardizations were repeated in every case until it was certain that the result was correct to 0.1 of one per cent. From these analyses the volumes of the two solutions which would contain the constituent salts in the same proportion in which they occurred in the double salt, were calculated. These volumes of the two solutions were mixed in a measuring flask and the whole diluted to a known volume. This solution, containing a mixture of the constituents of the double salt was then standardized gravimetrically, to see that no error had beed made in bringing the constituents together and in diluting them to a known volume. This standardized solution, which in every case was found to contain the constituent salts to almost exactly the extent which we had calculated, was used as the mother-solution. The more dilute solutions of this mixture were prepared from this mother-solution by diluting measured volumes in a measuring flask. In these cases, also, a number of the more dilute solutions were standardized directly.

In one or two cases the mother-solution of the mixtures was also prepared by bringing together weighed quantities of the dried salts, dissolving the mixture, and diluting to a known volume. In such cases the solution was also standardized gravimetrically. This method of preparing solutions of mixtures was simply used as a check on the method first described.

By preparing the solutions as above described I was confident that I knew the concentration of the double salt to 0.1 of one per cent, and I was equally confident that I had mixed the two salts in the same proportion in which they occur in the double salt, and had standardized the solution of the mixture to within about the same limit of error.

The same cell was used to measure the conductivity of the double salt as was used with the mixture. Some of the same water was used in making the solutions of the double salt and of the mixture of the constituents. Similarly, the same thermostat, thermometer, Wheatstone bridge, and resistance box

were always used in both cases. The cell was frequently restandardized, and temperatures (25°) were accurate to 0°.1. The conductivities of the solutions of double salt and of mixture were thus measured under as nearly the same conditions as possible. It now remains to be seen what results were obtained.

Double Chloride of Potassium and Cadmium,
$KCl.CdCl_2$.

The volumes are tabulated under v, the molecular conductivities under μ_v. All measurements were made at 25°.

	Double salt, $KClCdCl_2$.	Mixture of $KCl + CdCl_2$.	
v.	μ_v.	μ_v.	Difference.
2	117.8	119.4	1.6
4	146.3	148.1	1.8
8	172.4	174.9	2.5
20	208.4	209.3	0.9

The conductivity of the double chloride is, thus, less than the conductivity of the mixture of the two chlorides. The difference in this case is always small, but is larger than any known experimental error, and is always on the same side; *i. e.*, the mixture at all of the dilutions studied, has the higher conductivity. The difference here is, however, so small that if this was the only case studied it would arouse no special interest. Other cases have, however, been studied.

Double Sulphate of Potassium and Nickel,
$K_2SO_4.NiSO_4$.

The volumes at which the conductivities of the double salt and the mixture were measured are slightly different in this case. The values actually found were:

	Double salt, $K_2SO_4.NiSO_4$.		Mixture of $K_2SO_4 + NiSO_4$.
v.	μ_v.	v.	μ_v.
5.836	212.80	6	216.31
11.672	243.08	12	246.61
23.344	271.46	24	276.02
58.36	313.38	60	314.35
116.7	346.00		

The following comparison is made at the volumes of the

mixture, and the conductivities of the double salt at these volumes obtained by interpolation.

	Double salt, $K_2SO_4.NiSO_4$.	Mixture of $K_2SO_4 + NiSO_4$.	
v.	μ_v.	μ_v.	Difference.
6	213.68	216.31	2.63
12	244.38	246.61	2.23
24	273.31	276.02	2.71
60	314.13	314.35	0.22

The difference here is somewhat larger than in the case of the double chloride, and is again always on the same side; *i. e.*, the conductivity of the double salt is always smaller than that of the mixture at the same concentration. The difference here tends to grow less with increase in dilution, and it looks as if it might entirely disappear at greater dilutions.

Double Sulphate of Ammonium and Magnesium,
$(NH_4)_2SO_4.MgSO_4$.

The volumes at which the conductivities of the double salt were measured were different from those for the mixture. The following results were obtained:

	Double salt, $(NH_4)_2SO_4.MgSO_4$.		Mixture of $(NH_4)_2SO_4 + MgSO_4$.
v.	μ_v.	v.	μ_v.
1.608	149.7	2	164.6
3.216	189.8	4	202.4
6.432	224.8	8	237.1
16.08	265.6	20	277.9
32.16	298.6		

Interpolating the conductivities of the double salt for the volumes at which the mixture was studied, we have:

	Double salt, $(NH_4)_2SO_4.MgSO_4$.	Mixture of $(NH_4)_2SO_4 + MgSO_4$.	
v.	μ_v.	μ_v.	Difference.
2	159.7	164.6	4.9
4	197.7	202.4	4.7
8	231.5	237.1	5.5
20	273.9	277.9	4.0

The differences here are larger than in either of the other cases investigated, and again show that the double salt has a smaller conductivity than the mixtures of its constituents.

The differences in this case remain practically constant with change in dilution, but the greatest dilution used is not very high, and it might be that the difference would disappear in this case also with higher dilutions.

From these results we are led to the conclusion that the conductivity of a double salt in concentrated solutions is slightly less than the conductivity of a mixture of the constituents having the same concentration as the double salt. It looks as if the double salt, when once formed, did not dissociate in exactly the same way or to the same extent as the mixture of the constituents which had never united to form the double salt. This conclusion was so different from what we should expect that it was decided to test it in another way. The conductivity of a solution of the mixed salts was determined and a measured volume of the mixture then placed in a platinum dish and evaporated to dryness. Under these conditions there would be at least some of the double salt formed. This residue was then dissolved in some of the same pure water in which the mixture of the two salts was originally dissolved, and diluted to exactly the same volume. If the double salt has a smaller conductivity than the mixture of the constituents at the same dilution, the second solution containing the residue from the evaporation should have a smaller conductivity than the original solution of the mixtures at the same concentration.

The experiment was tried with the double sulphate of potassium and nickel. A solution containing the two sulphates in equimolecular quantities was evaporated nearly to dryness in a platinum dish, the residue dissolved and diluted to exactly the original volume. The volume of the solution was 24 liters. The following results were found :

$$K_2SO_4 + NiSO_4.$$

v.	
24 μ_v of mixture before evaporation	276.02
" " " " after "	274.59
" " " double salt	273.31

In a second experiment a more concentrated solution was employed, where $v = 12$.

12 μ_v of mixture before evaporation	246.61
" " " " after "	245.14
" " " double salt	244.38

In both of these experiments the mixture before evaporation had a larger conductivity than after evaporation. This agrees exactly with what was found above, since in the process of evaporation some of the double salt was formed by a union of the constituents. It will be observed that the mixture, after evaporation, had a larger conductivity than the solution of the double salt of the same concentration. This is also what is to be expected since, in the rapid evaporation, only some of the double salt was formed. Indeed, it could be readily observed with the eye that the residue, after evaporation, was a mixture of the double salt and the constituent sulphates.

These experiments confirm, then, the results of the direct measurement of the conductivities of double salts and of mixtures of their constituents. In concentrated solutions, at least, the mixtures have the higher conductivity.

In conclusion, I wish to express my thanks to Dr. H. C. Jones, at whose suggestion this investigation was undertaken and carried out.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY.

Contributions from the Chemical Laboratory of Lehigh University.

V.—THE ACTION OF SULPHURIC ACID ON PHENETOL.[1]

BY WILLIAM B. SCHOBER AND HENRY L. BOWERS.

The published statements of the different observers who have studied the action of sulphuric acid on phenetol (ethylphenyl ether) are not in accord, probably because the experimental conditions were not the same. Opl and Lippmann[2] heated pure phenetol, boiling at 168° to 170°, with an equal weight of English sulphuric acid on a water-bath for an hour and a half. They obtained two isomeric sulphonic acids,

[1] From the thesis of Henry L. Bowers, submitted to the Faculty of Lehigh University for the degree of Analytical Chemist, June, 1900.

[2] Ztschr. Chem, 1869, 470.

named by them phenetolsulphonic acid and phenetolparasulphonic acid, and found that the barium salt of the former was difficultly soluble in hot water, while that of the latter dissolved easily in cold water.

Moody[1] finds that, contrary to the statements of Kekulé, and Opl and Lippmann, anisol and phenetol, when treated with sulphuric acid, yield *only* the parasulphonic acid. He says: "phenetol like anisol on sulphonation either with sulphuric acid or chlorsulphuric acid, either warm or in the cold, gave rise only to the para acid." Lagai[2] controverted Moody's statement and asserted that he had isolated a second acid from the product obtained on sulphonating phenetol; he described its amide as crystallizing from water in feathery needles melting at 142°, but he gave no analyses or other evidence to show that it was a derivative of phenetol. Moody, by an indirect method, prepared the amide of orthophenetolsulphonic acid. It forms long flexible needles, melting at 156°.

One of us, several years ago, studied the action of sulphuric acid on anisol (methylphenyl ether)[3] under different conditions, and found that anisoldisulphonic acid was formed in every case in which the reacting substances were heated to 92°, the quantity increasing with an increase in the proportion of sulphuric acid and increase in time of heating.

Paranisolsulphonic acid was formed in every case, the amount decreasing with increase of temperature, time of heating, and excess of sulphuric acid.

Orthoanisolsulphonic acid was formed in small quantities when anisol and sulphuric acid were allowed to react at ordinary temperatures. It was not formed when the proportion (by weight) of sulphuric acid to anisol was greater than 4 : 1.

This investigation was undertaken for the purpose of studying the reaction between sulphuric acid and phenetol under varying conditions. The conditions of the experiments described below were so arranged that the results could be compared with those obtained in studying the action of sulphuric

[1] Proc. Chem. Soc., 1892, p. 90, 214.
[2] Ber. d. chem. Ges., **23**, 3392.
[3] This JOURNAL, **18**, 858.

acid on anisol. In this way the difference or similarity in behavior of the two ethers toward sulphuric acid will be shown.

Other investigations are in progress in this laboratory having for their object the study of the action of sulphuric acid toward the higher members of that class of mixed ethers of which anisol and phenetol are the first two.

Experiment I.

In this and the other experiments, the phenetol used was Kahlbaum's preparation, a clear, colorless liquid boiling constantly at 172°; the sulphuric acid was "concentrated chemically pure."

Fifteen and two-tenths grams of phenetol and 15 grams of sulphuric acid were mixed and allowed to stand at the room temperature (21°) for three hours. When the acid was poured into the ether the liquid became faintly red and a slight evolution of heat was noticed. The reaction-mixture was cooled from time to time in order to prevent the temperature from rising above 21°. Upon pouring it into a large quantity of water, 5 cc. of phenetol separated out. This was removed, and the acid solution neutralized with barium carbonate. The barium sulphate was filtered off and washed repeatedly with hot water. The barium salt was converted into the sodium salt by precipitation with sodium carbonate, the barium carbonate thus formed was filtered off, and this was also repeatedly washed with hot water. The solution of the sodium salt was evaporated to dryness on a water-bath, and then heated to 110° in an air-bath. The dried product weighed 14 grams. This was ground to a fine powder and treated with phosphorus pentachloride. The action was so energetic that it became necessary to cool the vessel and to add the halide in successive small quantities. The resulting sulphonchloride was poured into water and washed several times; it possessed a pinkish color and remained liquid in presence of water at 21°. After being purified, a concentrated solution of ammonia was poured over it and the mixture allowed to stand. The conversion into the amide took place slowly. The reaction-product was evaporated to dryness on a water-bath. In order to obtain the amide free from ammonium chloride, the mass was

extracted with absolute alcohol. The alcohol was then evaporated off, the residue dissolved in hot water, and allowed to crystallize. Two substances were found; they were separated by fractional crystallization. The one melting at 149° was assumed to be paraethoxybenzenesulphonamide,[1] the other melting at 128°, the meta compound.

An analysis of the former gave the following results:

I. 0.2537 gram substance gave 0.4466 gram CO_2 and 0.1352 gram H_2O.

II. 0.3397 gram substance gave 0.3998 gram $BaSO_4$ (Carius method).

III. 0.1267 gram substance gave 0.1467 gram $BaSO_4$ (Carius method).

IV. 1.0206 grams substance gave 0.070447 gram N (Kjeldahl-Gunning method).

	Calculated for $C_6H_4\langle^{OC_2H_5}_{SO_2NH_2}$	Found. I.	II.
C	47.73	48.01	....
H	5.48	5.92	....
S	15.94	16.18	15.90
N	6.99	6.92	....

The second amide found melted at 128°. Delisle and Lagai,[2] and Franklin[3] give the melting-point of the metamide as 131°. In a previous investigation the melting-point of the metamide was found to be 126°.

A partial analysis of the amide gave the following results:

I. 0.2030 gram substance gave 0.0013905 gram N.

II. 0.2118 gram substance gave 0.2484 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{OC_2H_5}_{SO_2NH_2}$	Found.
N	6.99	6.85
S	15.94	16.11

Weight of paramide, 8.11 grams.

Weight of metamide, 0.9 gram.

[1] Lagai gives the melting-point of the para compound at 149°.

[2] Ber. d. chem. Ges., **23**, 3392.

[3] Dissertation, 1894.

Experiment II.

In this and the following experiments the method of procedure was the same as that given in Experiment I. 15.2 grams of phenetol and 15 grams of sulphuric acid were mixed and allowed to stand six hours; the temperature remained constant at 21°. When the reaction mixture was poured into water, 4 cc. of the ether separated out. Two amides were found.

Weight of the paramide, 7.84 grams.

Weight of the metamide, 0.60 gram.

Experiment III.

This was a repetition of the preceding experiment except that the reacting substances were allowed to stand nine hours at a temperature of 21°. On pouring the mixture into water, 4 cc. of the ether separated out. Two amides were found.

Weight of the paramide, 8.0 grams.

Weight of the metamide, 0.59 gram.

Experiment IV.

15.2 grams of phenetol and twice the weight of sulphuric acid—30 grams—were mixed and heated on a steam-bath for thirty minutes. The temperature of the mixture during the heating was 90°. Two amides were found.

Weight of the paramide, 11.40 grams.

Weight of the metamide, 0.52 gram.

Experiment V.

The same quantities of phenetol and sulphuric acid used in the preceding experiment were mixed and heated on a steam-bath for sixty minutes. Temperature of the mixture during heating, 90°. Two amides were found.

Weight of the paramide, 10.27 grams.

Weight of the metamide, 0.46 gram.

Experiment VI.

This is a repetition of the two preceding experiments. The conditions were the same except the length of time—ninety minutes. The dried sodium salt obtained was decidedly pink in color. In the other experiments it was white. Two amides were found.

Weight of the paramide, 9.07 grams.
Weight of the metamide, 0.65 gram.

Experiment VII.

15.2 grams of phenetol and 60 grams of sulphuric acid were mixed and heated on a steam-bath for thirty minutes at a temperature of 90°. The dried sodium salt was pink. Two amides were found.

Weight of the paramide, 11.30 grams.
Weight of the metamide, 1.45 grams.

Experiment VIII.

The same quantities of the ether and acid as in Experiment VII were treated in the same way, except that the time of heating was twice as long—sixty minutes. The reaction-mixture assumed a deep reddish-brown color. The dried sodium salt was of a deep pinkish color. The sulphonchloride was dark-brown and solid at 22°. The solution of ammonia acted upon it slowly. The water into which the reaction-product, resulting from the treatment of the sodium salt with phosphorus pentachloride, was poured, yielded, upon evaporation, a considerable quantity of phenol. Small quantities of a dark-colored, gummy substance appeared during the crystallization of the amides. We were unable to obtain it in a pure condition. Two amides were found.

Weight of paramide, 3.10 grams.
Weight of metamide, 0.12 gram.

Experiment IX.

This is a repetition of Experiment VII, except that the time of heating was three times as long—ninety minutes. The sulphonchlorides formed a dark-colored, gummy mass, solid at 22°, which was apparently partially decomposed when treated with water. As in the preceding experiment, phenol was obtained on evaporating the water into which the sulphonchloride mixture had been poured.

Weight of the paramide, 1.96 grams.

If any of the metamide was formed it was impossible to obtain it pure, due to the presence of a considerable quantity of the gummy substance.

Experiment X.

This experiment was made in order to learn the effect of heating for a short time equal weights of phenetol and sulphuric acid. 15.2 grams of the ether and 15 grams of the acid were mixed and heated on a steam-bath for thirty minutes at a temperature of 90°. Two amides were found.

Weight of the paramide, 16.45 grams.
Weight of the metamide, 0.80 gram.

Experiment XI.

The same quantities of the ether and acid as in Experiment X were heated at the same temperature for twice the length of time—sixty minutes.

Weight of the paramide, 15.62 grams.
Weight of the metamide, 0.70 gram.

Experiment XII.

This was a repetition of Experiment XI. The time of heating, however, was ninety minutes. Two amides were found.

Weight of the paramide, 14.56 grams.
Weight of the metamide, 0.55 gram.

Experiment XIII.

In order to obtain a quantity of phenetoldisulphonic acid, 90 cc. of phenetol and the same volume of fuming sulphuric acid were mixed and heated on a water-bath at a temperature of 85° for thirty minutes. A portion of the reaction-product was converted into the amides. Four substances were found—the paramide in large quantity, exceedingly small quantities of the disulphonamide melting at 233°, a substance melting sharply at 189°, a substance melting at 142°. The last is undoubtedly the same compound that Lagai thought to be the orthoamide. Moody and Franklin give the melting-point of the orthoamide as 156°.

It is worthy of note that under the same conditions as those just given anisol forms a disulphonic acid with ease.

Summary of Results.

Experiment No.	Weight of acid.	Weight of phenetol.	Time of heating.	Temperature.	Weight of paramide.	Weight of metamide.
			Hours.			
I	15	15.2	3	21°	8.11	0.90
II	15	15.2	6	21°	7.84	0.60
III	15	15.2	9	21°	8.01	0.59
			Minutes.			
IV	30	15.2	30	90°	11.40	0.52
V	30	15.2	60	90°	10.27	0.46
VI	30	15.2	90	90°	9.07	0.65
VII	60	15.2	30	90°	11.30	1.45
VIII	60	15.2	60	90°	3.10	0.12
IX	60	15.2	90	90°	1.96	...
X	15	15.2	30	90°	16.45	0.80
XI	15	15.2	60	90°	15.62	0.70
XII	15	15.2	90	90°	14.56	0.55

Conclusions.

Paraphenetolsulphonic acid was formed in every case in which sulphuric acid and phenetol were mixed and allowed to stand at the ordinary temperature or heated, the amount decreasing with the length of time the two substances were allowed to react at a temperature of 90°. At the ordinary temperature, the length of time the substances were allowed to react seemed to exert no appreciable influence.

When the proportion of sulphuric acid to phenetol was greater than 1 : 1 the amount of the paraphenetolsulphonic acid decreased with the increase in length of time of heating the reacting mixture.

Metaphenetolsulphonic acid was formed in every experiment but one—No. IX, in which the proportion of sulphuric acid to the ether was 4 : 1, and the time of heating ninety minutes. The figures obtained are to be regarded as only fairly accurate, owing to the small quantities in which the meta acid was formed and the great difficulty of freeing the metamide from a gummy impurity.

Phenetoldisulphonic acid was obtained when equal volumes of phenetol and fuming sulphuric acid were mixed and heated for thirty minutes at 85°. The quantity was minute.

SOUTH BETHLEHEM, Pa.

NOTES.

The New Radio-active Substances.

Since the last note on polonium and radium appeared in this JOURNAL, considerable work has been done on radio-active substances in general.

Debierne[1] found in the residues of pitchblende a new radio-active substance, differing from polonium and radium, and closely allied, as he thought, to titanium in its chemical properties. More recent work,[2] however, has led him to believe that it does not resemble titanium in all its reactions. The most active specimen of this new substance which he obtained consisted largely of thorium, as was shown by its chemical reactions, as well as by its spectrum analysis, and yet it does not resemble thorium in all of its reactions. Debierne calls it actinium. The rays from actinium possess the same properties as those of radium. They cause barium platinocyanide to fluoresce, produce photographic impressions and effect the ionization of gases. He thinks that the radio-activity of thorium compounds is due to the presence of minute quantities of actinium, and that thorium itself is inactive. Debierne[3] has also succeeded in producing induced radio-activity by precipitating barium sulphate in the presence of actinium, but found that it differed from radiferous barium sulphate in that the former showed no radium lines in its spectrum, and further, the activity of the former decreases in time and is finally lost, while that of the latter increases to a certain point and then remains constant.

Stoutt,[4] Becquerel,[5] and others have been working on the effect of a magnetic field on the Becquerel rays. The Becquerel rays in general are deflected in a magnetic field, while the Roentgen rays are not, and further, Becquerel showed that the rays emitted by a specimen of polonium nitrate are not deflected in a magnetic field as are those emitted by radium. In the case of radium some of the rays are deviated while others are not.

Curie[6] has proved experimentally that the deviable rays of radium are due to material emissions from the source of activity. He found that the emissions from radium charge bodies which receive them negatively, while the radium itself is charged positively. The non-deviable rays of radium seem

[1] Compt. rend., **129**, 593.
[2] Chem. News, **81**, 169.
[3] Compt. rend., **131**, 333.
[4] Chem. News, **81**, 61.
[5] *Ibid.*, **81**, 121.
[6] *Ibid.*, **81**, 145.

to be of a different kind from the deviable rays or they have lost their electric charges. It has been urged against the material emission theory that if it be correct the radium emitting the rays ought to lose in weight, but it would be practically impossible to measure the loss in weight of radium due to emissions, because it has been calculated that it would require a million years for a specimen of radium to lose one milligram in weight. Debierne[1] found that the rays from actinium, like those from radium, are partly deviated in a magnetic field, and are charged negatively.

Bary[2] has carried on investigations with the view of determining what metals show luminosity in their salts under the influence of Becquerel rays. He found that such metals are lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, and barium. Of other metals, only the phosphorescent salts of uranium showed fluorescence. The author concluded that the same class of bodies which give salts phosphorescent to light also give compounds which are luminous under the influence of Becquerel rays. He regards the permanent luminosity of radio-active barium as due to the influence of Becquerel rays on the barium salt. But since the chemical properties of radium and barium are so similar, it may be that pure radium salts are fluorescent in the same manner as other metals of this class.

Demarçay[3] has recently again examined the spectrum of radium. The material was furnished him by Mdme. Curie and consisted of nearly pure radium chloride. He was unable to find any lines which were not present in his first spectral analysis of a more impure radium chloride, although the lines particularly characteristic of radium were much more intense than they were when previously observed.

Mdme. Curie[4] has redetermined the atomic weight of radium, using a specimen of radium chloride, which, to judge from the appearance of its spectrum, was but little less pure than the specimen which was furnished Demarçay for his spectrum analysis. The atomic weight was determined by estimating the chlorine in the anhydrous chloride of radium. In two determinations the results were 174.1 and 173.6. Since the specimen of chloride contained some barium chloride, the atomic weight of pure radium is doubtless considerably higher.

Giesel[5] has succeeded in obtaining a small amount of Debierne's actinium. He treated a concentrated solution of

[1] Chem. News, **81**, 169.
[2] *Ibid.*, **81**, 157.
[3] *Ibid.*, **82**, 73; Compt. rend., **131**, 258.
[4] Chem. News, **82**, 98; Compt. rend., **131**, 382.
[5] Ber. d. chem. Ges., **33**, 1665.

uranium nitrate with a small amount of a soluble barium salt and sulphuric acid. The resulting precipitate of barium sulphate was strongly radio-active, while the uranium nitrate had lost most of its radio-activity. The active barium sulphate, after conversion into a soluble barium salt, was treated with ammonia, and a small quantity of a very active substance was precipitated, while the remaining barium salt had lost its activity entirely. Radium could not have been separated from barium by ammonia, but actinium could, so Giesel concluded that the final radio-active substance which he obtained was a derivative of actinium.

He also endeavored to separate polonium from bismuth, but in this was unsuccessful, and thinks that the so-called polonium is only a radio-active form of bismuth. He found the 0.5 gram of polonium, obtained from 500 kilograms of uranium residues, to consist entirely of bismuth hydroxide, $Bi(OH)_3$, which is also strongly radio-active, as is the oxychloride, BiOCl.

Several attempts have been made to determine whether radio-active uranium compounds can be rendered inactive by a transference of their radio-activity to other substances.

Becquerel,[1] by repeatedly treating uranium salts with barium chloride and precipitating the barium as sulphate, was able materially to decrease the radio-activity of the uranium salts, but could not make it disappear altogether.

Crookes[2] has been more successful. Since radium resembles barium so closely, he examined a large number of barium minerals, with a view of finding some of them containing radium, but all that he examined were inactive. He then examined a number of rare minerals, and found only those radio-active which contained thorium and uranium. The different salts of uranium showed about the same radio-activity.

It was possible, starting with a uranium nitrate which was strongly radio-active, to obtain by repeated crystallizations a nitrate which is entirely inactive, even though modifications in the physical or chemical conditions of the salt did not affect its radio-activity. Crookes showed that, when uranium nitrate is treated with ether, the portion which is dissolved by the ether shows no radio-activity, while the insoluble portion is much more strongly radio-active than the original salt.

He showed further that the radio-active substance in uranium can be precipitated by ammonia. When a solution of uranium nitrate is treated with ammonia, all the radio-active substance is found in the precipitate. He designates this radio-active substance found in uranium and its salts as UrX,

[1] Compt. rend., **130**, 1583; **131**, 137.
[2] Chem. News, **81**, 253.

which differs from polonium in that it is not volatile, while polonium is; and further the rays from UrX will pass through aluminium, lead, and glass, and those from polonium will not. Again, polonium is precipitated by hydrogen sulphide and UrX is not. UrX and radium also differ in many chemical properties, and Crookes thinks they are different substances, although he could not photograph lines in the spectrum of his UrX, because it was too weak. It is possible that his UrX and Debierne's actinium are identical. He thinks that radio-active thorium compounds can also be separated into inactive thorium and an active substance.

Quite recently, Hofmann and Strauss[1] have succeeded in isolating radio-active lead salts and radio-active rare earths from uranite, pitchblende, bröggerite, cleocite, samarskite, and euxenite. In the products which were obtained it was impossible to detect traces of uranium, thorium, polonium, radium, bismuth, barium, or titanium. It seems particularly interesting that radio-active substances should have been obtained from bröggerite, which was absolutely free from uranium and thorium. These authors have also confirmed the work of Crookes in obtaining entirely inactive uranium from a strongly radio-active specimen. C. E. C.

On the Nature of the Oxyazo-Compounds.

In my article "On the Nature of the Oxyazo-Compounds" printed in this JOURNAL (Vol. **22**, 364), the statement is made that the free paraoxyazo compounds do not react with phenylhydrazine. I find, however, that when paraoxyazobenzene is heated to 100° with an excess of phenylhydrazine, a slow decomposition occurs attended by the evolution of nitrogen and the formation of a white, crystalline body. Other oxyazo compounds under the same conditions show a similar action. This reaction is now being studied in this laboratory.

OHIO STATE UNIVERSITY,
December 15. WILLIAM MCPHERSON.

REVIEWS.

CHEMICAL TECHNOLOGY, or Chemistry in its Applications to Arts and Manufactures, edited by CHARLES EDWARD GROVES, F.R.S., and WILLIAM THORP, B.Sc.; VOL. III, GAS LIGHTING, by CHARLES HUNT, Manager of the Birmingham Corporation Gasworks. Philadelphia: P. Blakiston's Son & Co. 1900. pp. xviii + 312.

The first volume of this work was devoted to "Fuel and Its Applications," treated of by E. J. Mills and F. J. Rowan, and was published in 1889 in England and the United States.

[1] Ber. d. chem. Ges., **33**, 3126.

The second volume, on "Lighting by Solid and Liquid Illuminants," by W. Y. Dent, J. McArthur, L. and F. A. Field, B. Redwood, and D. A. Louis, appeared in 1895. It was announced that the third volume would include the subjects of "Gas Lighting, Electric Lighting, Lighthouse Illuminations, and Photometry," but of these the first only appears in the volume now issued. In general plan and character it much resembles those that have preceded it. There is presented a large mass of valuable information, not very well ordered or marshalled, and rather unequal in regard to the fulness of detail of different parts of the subject. In a monograph aiming at completeness one might fairly expect to find, not merely numerous analyses of British gas coals, but like analyses of the materials in use in other countries. The production in France of illuminating gas from the "suint" of wool washing is not mentioned at all, nor is there any notice of rosin or wood gas; a few pages are given to the manufacture of "oil gas" from hydrocarbon shale oil (not the original oil gas of the early part of this century, from which Faraday first obtained benzene), but arrangements tried in the United States for making gas from petroleum are not noticed. Among the most valuable chapters are those on modern types of regenerative furnaces for heating coal-gas retorts, on machinery for charging the retorts and withdrawing the coke from them, and on gas burners, including regenerator and incandescent burners. In connection with the last named appliances one misses the interesting results of v. Welsbach's investigation of the character (color) of the light from mantles prepared with the various rare earths which he has brought into use. Acetylene from calcium carbide is inadequately treated; much of the knowledge in regard to it, and to the conditions for its safe employment, which has been acquired within the last few years should have been collated and discussed. A number of subordinate points in the book are quite interesting, for example, the question of the circumstances affecting the formation of naphthalene deposits in coal-gas mains. As a whole, the work should find a place in every general collection of technological literature. J. W. M.

L'EAU DANS L'INDUSTRIE, par H. DE LA COUX, ingénieur-chimiste expert près le Conseil de Préfectur de la Seine, etc. Paris: Vve. Ch. Dunod. 1900. pp. 496.

Many of the modern technical works on water supply devote a chapter or so to the relations of water to special manufactures, but usually the space so used is small, and the subject is treated in a very condensed and general way. The book now noticed does not discuss the general use of natural

waters for drinking and other domestic purposes, but is concerned altogether with industrial applications. It is a well-arranged and valuable manual—not absolutely exhaustive, but on the whole satisfactorily covering the field proposed. It contains an extensive, detailed, and well-illustrated discussion of boiler incrustation and boiler corrosion, both in relation to ordinary fresh waters and also to sea water and the waters from mines, the means of dealing with such troubles, different types of boiler, preheating arrangements, chemical treatment of the water, etc. The special considerations are gone over which affect the use of water for soap-making, washing on the industrial scale, flax steeping, wool cleansing, bleaching, dyeing, tanning, paper-making, photography, sugar refining, brewing, distilling, etc. Means and apparatus are described for the purification of water intended for various special purposes, including filters, filter presses, and other mechanical appliances. There is an extended discussion of the treatment of residual watery liquids from various sources, mixed sewage, soapy water, and the recovery from it of glycerol. The book closes with chapters on analytical methods, qualitative and quantitative. There are numerous and generally good illustrations accompanying the text. Like most French scientific books, it has a good table of contents at the end, but no index. J. W. M.

THE OIL CHEMIST'S HANDBOOK. By ERASTUS HOPKINS, A.M., B.Sc., Chemist in charge of U. S. Laboratories, Boston, Mass. New York: John Wiley & Sons. 1900. pp. viii + 72.

This book is intended to present, in condensed form, the chief approved methods for testing fixed oils, fats and waxes for commercial purposes—hydrocarbon oils are only considered in their relations as adulterants. The descriptions of analytical processes are much too brief to guide safely anyone depending upon the book for instruction, and in some cases they are altogether inadequate, as, for example, in the few lines devoted to the quantitative determination of glycerol.

The tables in which the fats and oils are arranged, not alphabetically, but in the order determined by particular reactions, such as the saponification value, are convenient. More exact references to the authorities for individual results would have added to the usefulness of these tables. There are some statements of value in regard to special methods of adulteration.

The very brief discussion of points involving general chemical principles is marked by, to say the least, loose and unfortunate expression, and the language of the book as English is not above criticism. J. W. M.

GRUNDLINIEN DER ANORGANISCHEN CHEMIE. Von WILHELM OSTWALD. Mit 122 Textfiguren. Leipzig: Verlag von Wilhelm Engelmann. 1900. pp. 795. 8vo.

At last a serious attempt has been made to present the subject of inorganic chemistry in the light of the results which have been achieved in the field of physical chemistry. Probably no one is better fitted for this work than the writer of the book before us. Certainly no one has done more to make a place for physical chemistry than Ostwald, so that this book will attract an unusual amount of attention, and it deserves much more than a passing notice. The first feeling experienced by one who, though not a physical chemist, is much interested in the work in progress in that field, is that of relief to find that so much is left of the old structure. In his preface the author says he has retained as much as possible of the old forms: "Was ich beibehalten habe ist zunächst die naturhistorische Anordnung des Stoffes. Mann könnte vielleicht schon jetzt den Versuch wagen, die Chemie von vornherein als eine rationelle Wissenschaft auf Grund einiger Prinzipien aufzubauen, und die Beschreibung der verschiedenen Stoffe als Erläuterungen dieser allgemeinen Gesetze einzuführen. Was mich hiervon abgehalten hat, ist nächst dem Bedürfnisse des geschichtlichen Zusammenhanges die Erkenntniss gewesen, dass die Mannigfaltigkeit der verschiedenen Stoffe zu gross und ihre Einzelkenntniss zu wichtig ist, als dass eine solche Darstellung gegenwärtig für den Unterricht sich verwerthen liesse." However objectionable it may appear, it is still necessary, and it is likely to remain necessary, to study things as well as the laws that govern their action upon one another. The author clearly recognizes this, and consequently he deals to as great an extent with *things* as others do. The old things are still there, and the old laws. Some of the old conceptions have, to be sure, been pushed into the background, and the view will not appear familiar to the majority of chemists.

The author has practically abandoned the atomic theory, Avogadro's hypothesis, and the Periodic Law. They are all mentioned but so that the student will get the impression that they are of little value. Thus, on page 155, he says: "Die Aufstellung der Atomhypothese in dem hier entwickelten Sinne ist im Jahre 1805 durch J. Dalton erfolgt; die Prüfung ihrer wichtigsten Konsequenz, des Gesetzes der Verbindungsgewichte, ist von Berzelius ausgeführt worden. Durch die vollkommene Uebereinstimmung derselben mit der Erfahrung hat die Atomhypothese ein grosses Ansehen und eine allgemeine Anwendung erlangt, so dass sie noch gegenwärtig in der Chemie nahezu ausschliesslich herrscht.

"Auch in diesem Buche soll von diesem allgemeinen Gebrauch nicht wesentlich abgewichen werden. Doch läge es sicher im Interesse der Wissenschaft, wenn in dieser Beziehung eine grössere Vorsicht beobachtet würde, und deshalb ist hier Wert darauf gelegt worden, die Ausdrucksformen der Atomhypothese so sparsam anzuwenden, als es der heutige Sprachgebrauch nur gestattet."

The same caution is shown in presenting the molecular hypothesis commonly called "Avogadro's law," and in place of the conception of *molecular weight* that of *normal weight* is used. The normal weight of a gas is the weight of a volume of the gas as compared with the weight of the same volume of a hypothetical gas, the weight of which is 1/32 of that of the same volume of oxygen.

The periodic law is not referred to until the end of the book is reached, when nine pages are devoted to it. Its imperfections are emphasized and then follows this passage, p. 775: "Fragt man, wie man sich diesen und ähnlichen Unvollkommenheiten des periodischen Systems gegenüber zu stellen hat, so ist zu sagen, dass es sich hier nicht um ein Naturgesetz im strengen Sinne handelt. * * * Wir kennen, um ein Bild zu brauchen, von dem grossen Organismus der chemischen Thatsachen nur einen gewissen, zum Theil willkürlich geführten Querschnitt, während der übrige Körper uns fast ganz fremd geblieben ist. Es darf uns daher nicht wundern wenn wir die den ganzen Organismus beherrschenden Gesetze an diesem zufälligen Querschnitt noch nicht zu übersehen vermögen."

While it is undoubtedly true that all the facts of chemistry can be represented without the aid of the atomic hypothesis, the molecular hypothesis, or the periodic law, it cannot be denied that these are of great assistance in dealing with the facts. The conceptions "normal weight" and "combining weight" are not as clear as molecular weight and atomic weight, though they appear to be free from speculation. Though the time may come when we shall be able to abandon the older conceptions, it will not come until we have something better to substitute for them. It does not seem to the reviewer that the conceptions that Ostwald makes use of are better.

The only danger in the atomic hypothesis is that which attaches itself to every hypothesis. Many will overwork it. For the clear thinker this danger does not exist, and there is no method of dealing with facts that will prevent the average student from going astray.

As regards the periodic law, is it not true that inorganic chemistry has become much more interesting since this law, however imperfect it may be, has been recognized? And is it

wise to throw away this advantage because of the imperfections of the law as we at present know it?

The chief interest in the book before us is connected with the introduction of the results of investigations in the field of physical chemistry. Ions pervade the book. Catalysis is often introduced to *explain* curious phenomena. The Law of Mass Action is presented by means of a few examples. The Phase Rule also comes in for its share of attention. There is no serious difficulty in presenting the conception of ions and showing the connection between this conception and facts that are constantly dealt with in the laboratory. There is, however, the same danger here that is presented by the atomic hypothesis. Ions can easily be overdone. It will hardly be claimed that the ion is entirely free from speculation. There is difficulty in making the Phase Rule and the Law of Mass Action clear in the early stages of the study of chemisty for the reason that the reactions that illustrate them best are not every-day reactions, and therefore, even after learning what the laws are, the student fails to see the connection between them and the phenomena he commonly has to deal with. No doubt the connection exists, but in most cases it cannot be recognized.

A careful examination of this book has not destroyed the impression that the incorporation of the conceptions of physical chemistry into a course in general inorganic chemistry involves grave difficulties. However heterogeneous the facts of inorganic chemistry may appear, we cannot disregard them. They must be mastered. Ostwald concedes this. Physical chemistry as such cannot take the place of what some call old-fashioned chemistry, but undoubtedly old-fashioned chemistry can be improved by physical chemistry, and all chemists owe a debt of thanks to Ostwald for his effort to show how this improvement can be brought about. Every chemist should own a copy of this book, and should conscientiously study it.

I. R.

ACETYLENE, A HANDBOOK FOR THE STUDENT AND MANUFACTURER. By VIVIAN B. LEWES F.I.C., Etc., Professor of Chemistry, Royal Naval College, Greenwich, Chief Superintending Gas Examiner to the Corporation of the City of London, etc., etc. With 228 illustrations. Macmillan Co. 1900. pp. 978.

The publication of this book fills a gap in chemical and technical literature, for despite the importance of the subject no handbook of acetylene existed in the English language, nor were the German and French text-books sufficiently comprehensive to satisfy the chemist, as all of them were written by engineers presenting the subject from the technical point of view. Professor Lewes is a chemist, a noted expert in the

chemistry and technology of artificial light, and has since the first introduction of acetylene done much work on its use as an illuminant. Indeed, the searcher for knowledge of acetylene has hitherto found the scattered articles of Lewes his most reliable source.

A handbook of acetylene must be available for the chemist, the technologist, the manufacturer, and the inventor. To this end the author divides his book into three parts.

Part I, Scientific (169 pages), gives in four chapters the history of acetylene, its preparation, its properties, its chemical reactions. Everything of importance bearing on the subject, even work of little apparent importance, will be found here. The treatment is clear and well-proportioned, and references to the original articles are everywhere given. The space given to the brilliant work of Berthelot, Vielle, Moissan, Haber and Oechelhausen, Gerdes, and others is ample, and the more important experiments and conclusions are given in the form of extracts from the original articles.

The following extract from Lewes's own work may be of interest: "Experiments made by withdrawing the gases from various parts of luminous flames show that no matter what is the initial character of the hydrocarbon present, acetylene is always produced before luminosity makes its appearance, and moreover that the illuminating power of the flame follows the ratio of acetylene so produced; and this fact, taken in conjunction with the observation that when acetylene free from air is allowed to flow through a Jena-glass tube heated up to a temperature of 780° C., it is decomposed with luminosity, whilst the carbon set free in flowing forward through the zone of heat is perfectly non-luminous, formed the basis of what is now known as the acetylene theory of luminosity.

"Stated in its simplest form, this theory is as follows: In the same way in which the decomposition of the acetylene in flowing through a heated tube endows the carbon particles with a luminosity which the heat of the tube alone is unable to impart, so does the decomposition of the acetylene generated in a hydrocarbon flame increase the light-yielding power of the carbon particles liberated by its decomposition over what might have been the light emitted had they only been heated to the temperature of the flame itself. * * * * Lewes gives the temperature of decomposition of acetylene as 780° C., whilst Haber places it between 770° and 790° C. Frank, however, gives it as above 1000°, though upon what evidence is not clear." This subject, in its practical bearings, is discussed historically and fully in a later chapter.

Part II, Technical (489 pages), describes in seven chapters the electric furnace and its application to calcium carbide (33

electric furnaces are described); the manufacture, properties, and impurities of calcium carbide; the generation of acetylene; the impurities of commercial acetylene; and the processes adapted for their removal; the generation of light and power from acetylene; the utilization of diluted acetylene; the analysis of material for carbide manufacture; and of carbide and acetylene.

Those who have paid little attention to the acetylene industry will be surprised at the bewildering number of furnaces, methods, generators, lamps, and burners offered to the public. Only a skilled technologist can find his way through this maize. The author groups the furnaces, generators, etc., into types, shows by experiment the relative advantages of each type, and points out wherein the individual inventions are better or worse than their type average.

The chapter on the utilization of diluted acetylene is of particular interest, especially as more than half of the acetylene made abroad is not burned pure, but is used for enriching Pintsch gas for car illumination on the German railways, and has been recently introduced on the English railways. It will be remembered that the attempt was made in this country a few years ago to enrich water-gas with acetylene, and that the attempt failed; it was found that nearly 24 per cent of acetylene is required to enrich non-luminous water-gas to the average illuminating value, the mixture of hydrogen and carbon monoxide having the effect of practically destroying the illuminating power of acetylene. At the same time it was found that additions of acetylene to poor *carburetted* water-gas developed the theoretical enrichment value of the former. In investigating this and some similar phenomena, Lewes's experiments proved that of the so-called diluents, methane is the only one capable of developing the great illuminating or enrichment value of acetylene, and that it is to the presence of methane in poor coal-gas and in poor carburetted water-gas that the enrichment caused by small additions of acetylene is due.

This led Lewes to devise an ingenious method for charging water-gas with methane at slight cost, the product enriched with small percentages of acetylene being an illuminating gas of good average candle power.

Part III includes the legal enactments in force in various countries with regard to the use of acetylene, and a list of English patents of generators and burners with brief descriptions of each. The patent list occupies 147 pages with an average of five patents to a page, making over 700 patents.

In conclusion it may be noted that while the reader marks with regret the utilization of so many of the beautiful waterfalls of Europe for generating electric power, bringing as it does

the desecration of the most hidden and beautiful nooks by factory and workman's village, still the movement of branches of industry dependent on electric current or employing cheap power from the seaboard and plain to sparsely populated mountain districts is of interest and indeed of the greatest importance in the distribution of wealth and population. This movement has been developed chiefly hitherto by the carbide industry; thus Spain and Norway are absorbing capital which is to change lone mountain regions into manufacturing centers.

The publishers should be congratulated on this well printed and lavishly illustrated volume. E. R.

COMMERCIAL ORGANIC ANALYSIS. By ALFRED H. ALLEN, F.I.C., F.C.S. Volume III, Part I; TANNINS, DYES, AND COLORING MATTERS, WRITING INKS. Third edition, revised and enlarged, by J. MERRITT MATTHEWS, PH.D., Professor of Chemistry and Dyeing in the Philadelphia Textile School. Philadelphia: P. Blakiston's Son & Co. 1900. pp. xvi + 589. Price $4.50.

The revision of this volume has greatly increased its usefulness. The section on tannins is enlarged by the description of some new tannin materials and several new methods of analysis. The chapter on Dyes and Coloring Matters has undergone considerable change, as might be expected, considering the great number of dyes that have come into use since the second edition of this work was printed. The dyes have been reclassified in a better way, the chapter rewritten in part, and descriptions of a great many new dyestuffs included in the tables. The analytical tables have also been amplified, and new tables added. Many new dyes are described in the text, but more could very well have been added, with elimination of some dyes now unimportant, which are retained from the older volume.

Minor defects are present, as might be expected. The footnotes often run over to another page; many of them could have been incorporated in the text, with greater comfort to the reader. The method of rendering substantive cotton colors faster to washing and light by diazotizing and developing with phenols or amines does not receive the notice that its importance deserves. The second formula for tartrazin on page 139 has two SO_3Na groups missing. The formula $C_6H_5.N:N.Cl$ and the name diazobenzene chloride (page 142) is retained, instead of $C_6H_5.\overset{\overset{N}{\|}}{N}.Cl$, diazonium chloride. Other cases might be cited where the revision has not been carried far enough.

This edition is in general "up-to-date," and those who deal with dyes will find it advantageous to put it in the place of the corresponding volume of the second edition of this work.

G. S. F.